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OF

APPLIED CHEMISTRY

VOL. I.

A DICTIONARY

OF

APPLIED CHEMISTRY

BY

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ASSISTED BY EMINENT CONTRIBUTORS

VOL. I.

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WITH ILLUSTRATIONS

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PREFACE

THE publication of the present edition of this work has been delayed by circumstances arising out of the Great War. Some of those who contributed to previous editions were actively engaged as combatants; others were employed in munition work or in industries closely associated with such work, and consequently were unable to find time or opportunity to revise their articles until the conclusion of hostilities. Some valued contributors were no longer with us, and it was necessary to make fresh arrangements in regard to new writers. Provision also had to be made for additional articles necessitated by the development of chemical industry since the date of the previous edition. From the fact that practically the whole chemical energies of the country were concentrated on the prosecution of the war it was impossible to make rapid progress with the revision of a work of this magnitude.

It has become a truism to say that Applied Chemistry has exercised a profound influence on the character and direction of the war. It is equally true that the war has exercised a great influence on Applied Chemistry. It has led to an enormous expansion, more or less permanent, of certain branches, both in this country and abroad. New products have been made, new processes have been devised, and established methods have been improved and extended. In spite of the economic and other evils which have followed in its train, there can be no doubt that the war will be found to have permanently affected for good the progress of manufacturing chemistry in this country, and indeed in all English-speaking countries. Whilst the disturbance and strain of the past half-dozen years have seriously affected the development of pure science and the output of chemical research, Applied Chemistry has been quickened in certain directions. The financial and industrial collapse which has overthrown our late enemies will, it may be presumed, tend still further to accelerate the expansion of our own chemical manufactures. Germany, for the present at all events, no longer holds the supreme position in certain branches in chemical industry that she enjoyed prior to 1914, and it may be doubted whether, under her altered social and economic conditions, she will ever recover it.

It is too soon to be in a position to chronicle all the results, as regards chemical manufacture, which have arisen from the intensive application of chemists during the past strenuous years. Much is of a character that in the present disturbed state of the world it would be inexpedient to make public. On certain matters, indeed, no authoritative information can be obtained. This will explain why manufacturing details of several new processes in connection with munitions have not been given.

The entire work has been carefully revised, and so much new matter included that it has been found necessary to enlarge it, and six volumes will certainly be needed, and it is possible that a seventh will be required. It is to be hoped that in its present form the book may still be considered as a reasonably adequate presentation of the state of contemporary knowledge concerning the applications of Chemical Science.

A list of the contributors, with the titles of their articles, is prefixed to the several volumes. Their names and standing are a sufficient guarantee that, as in previous editions, every effort has been made to make the Dictionary a faithful record of the present relations of chemistry to the arts and sciences.

ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Annalen der Chemie (Justus Liebig).
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim.	Annales de Chimie.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur.	Annales de l'Institut Pasteur.
Ann. Physik.	Annalen der Physik.
Ann. Physique	Annales de Physique.
Annali Chim. Appl.	Annali di Chimica Applicata.
Apoth. Zeit.	Apotheker-Zeitung.
Arch. Pharm.	Archiv der Pharmazie.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Bentl. a. Trim.	Bentley and Trimen. Medicinal Plants.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt fur Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch	Biochemische Zeitschrift.
Brewers J.	Brewer's Journal.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Chem. Ind.	Chemische Industrie.
Chem. News	Chemical News.
Chem. Soc. Proc.	Journal of the Chemical Society of London. Proceedings.
Chem. Soc. Trans.	Journal of the Chemical Society of London. Transactions.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Färber-Zeit.	Farber-Zeitung.
Flück. a. Hanb.	Fluckiger and Hanbury. Pharmacographia.
Frdl.	Friedlander's Fortschritte der Teerfarbenfabrikation.
Gazz. chim. ital.	Gazzetta chimica italiana.
Helv. Chim. Acta	Helvetica Chimica Acta.
Jahrb. Min.	Neues Jahrbuch fur Mineralogie, Geologie und Palaeontologie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Bd. Agric.	Journal of the Board of Agriculture.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Phys. Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers.	Journal of the Society of Dyers and Colourists.
J. Tokyo Chem. Soc	Journal of the Tokyo Chemical Society.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Kolloid Zeitsch.	Kolloid-Zeitschrift.
Met. & Chem. Eng.	Metallurgical and Chemical Engineering.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pharm. J.	Pharmaceutical Journal.
Pharm. Zeit.	Pharmaceutische Zeitung.

ABBREVIATIONS OF THE TITLES OF JOURNALS AND BOOKS.

Phil. Mag. . . .	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans. . . .	Philosophical Transactions of the Royal Society.
Phot. J.	Photographic Journal.
Proc. Roy. Soc. .	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Rec. trav. chim. . .	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Nahr. Genussm. . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

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DICTIONARY

OF

APPLIED CHEMISTRY

AAL, A'L, ACH, AI'CH. Native names for the roots of *Morinda tinctoria* and *M. citrifolia*, employed in various parts of India, under the general trade name of Suranji, as a dyestuff, more especially for dyeing reds, purples, and chocolates.

ABACA. A species of fibre derived from *Musa textilis* (Née), obtained mainly from the Philippine Islands, and used in the manufacture of mats, cordage, &c. It is also known under other names, including 'Manilla hemp,' 'Menado hemp,' 'Cebu hemp,' 'Siam hemp,' and 'White rope.' Less valuable fibres are obtained from other species of *Musa*, such as *M. sapientum* (Linn.), the banana and plantain, which yield banana fibre and plantain fibre.

ABANONE. Trade-name for a pharmaceutical preparation of magnesium phosphotartrate.

ABIES. The generic name of the Silver Firs. *A. alba* (Mill.) [*A. pectinata* (DC.)] furnishes timber very similar to the white deal of *Picea excelsa*, the common spruce. It is the source of 'Strasburg turpentine,' containing free *abienic*, *abietric*, and *α*- and *β-abietinolic acids*, and an amorphous substance *abietoresen*, an ethereal oil of agreeable aromatic odour, a bitter principle and colouring matter (Tschirch und Weigel, Arch. Pharm. 1900, 238, 411).

A. Canadensis is the source of Canada balsam, which contains *canadic*, *canadolic*, and *α*- and *β-canadinolic acids*, an ethereal oil, *canadoresen*; and small quantities of succinic acid and a bitter substance. The acids contain no methoxyl groups and give the cholesterol reactions, including that of Tschugaeff (*l.c.* 1900, 238, 487).

ABIETENE. A hydrocarbon obtained by distilling the terebinthinate exudation of *Pinus sabiniana* (Doug.), a coniferous tree indigenous to California, and growing on the dry slopes of the foothills of the Sierra Nevada and on the hills along the coast, and known locally as the Nut pine or Digger pine. To procure the exudation, the tree during winter is notched and guttered at a convenient height from the ground, and the resin on distillation yields the liquid hydrocarbon. The crude oil was met with in San Francisco as an article of commerce under the names of 'Abietene,' 'Erasine,' 'Aurantine,' and 'Thioline,' and was used for removing grease-spots, paint-stains, &c., from clothing. It is a nearly colourless mobile liquid of powerful aromatic smell, recalling that of oil of oranges.

Abietene has been shown by Thorpe to consist almost entirely of *normal heptane*, C_7H_{16}, mixed with a small quantity of a resin to which its characteristic smell of orange oil is due (Thorpe, Chem. Soc. Trans. 35, 296; Schorlemmer and Thorpe, Phil. Trans. 174, 269; *v.* also Blasdale, J. Amer. Chem. Soc. 1901, 162).

Schorger (J. Ind. Eng. Chem. 1913, 5, 971) has shown that the volatile oil of *Pinus jeffreyi* consists of about 95 p.c. of *n*-heptane and 5 p.c. of an aldehyde, apparently citronellal.

Abietene is also the name given to the hydrocarbon which is obtained as an oil by the reduction of abietic acid (*q.v.*) (Easterfield and Bagley, Chem. Soc. Trans. 1904, 1238; Kraemer and Spilker, Ber. 1899, 2953, 3614). Its formula is $C_{18}H_{28}$, and it is probably decahydroretene, as, when carefully purified, and reduced with phosphorus and hydriodic acid, it yields a fluorescent hydrocarbon identical with the dodecahydroretene of Liebermann and Spiegel (Ber. 1889, 780).

ABIETIC ACID. An acid obtained by digesting colophony with dilute alcohol and recrystallising the product from methyl alcohol (Maly, Annalen, 129, 54; 132, 249); or by saturating an alcoholic solution of colophony with hydrogen chloride and subsequently recrystallising the product (Flückiger, J. 1867, 727; *cf.* Cohn, Chem. Zeit. 1916, 40, 791). It can also be obtained by distilling colophony under reduced pressure or with superheated steam (Easterfield and Bagley, Chem. Soc. Trans. 1904, 1238). Natural colophony is, in fact, a vitreous modification of abietic acid. It occurs in resin spirit, from which it may be obtained by extraction with ether, shaking with sodium carbonate solution and then acidifying. It is obtained in a purer condition by recrystallising from acetic acid, forms colourless triangular plates; m.p. 166°-167° (Tschirch and Wollf, Arch. Pharm. 1907, 1; 153°-154° (Mach, Monatsh. 1893, 186; 150°-152° (Ellingson, J. Amer.

Chem. Soc. 1914, 36, 325). The melting-point appears to be influenced by the manner of heating. Occurs also in Storax. $[a]_D -57·5°$. According to Easterfield and Bagley and Mach, it is a derivative of phenanthrene, and has the formula $C_{19}H_{28}O_2$, whilst Levy (Ber. 1906, 3043), Koritschoner (J. Soc. Chem. Ind 1907, 641), Fahrion (J. Soc. Chem. Ind. 1907, 264), and Vesterberg (Ber. 1907, 120) represent its composition as $C_{20}H_{30}O_2$. According to Strecker (Annalen, 150, 131), Duvernoy (Annalen, 148, 143), and Easterfield and Bagley (*l.c.*), abietic acid is identical with sylvic acid; it is not identical with pimaric acid, which yields abietic acid on distillation under reduced pressure. By distilling abietic acid under ordinary pressure, or, better, by treatment with hydriodic acid, carbon dioxide is evolved, the hydrocarbon *abietene* $C_{18}H_{28}$ being formed (E. and B. *l.c.*, Levy, *l.c.*; Kraemer and Spilker, Ber. 1899, 3614). Oxidation with nitric acid yields dinitropropane and *trans*-cyclo-hexane 1 : 2-dicarboxylic acid. Distillation with sulphur converts abietic acid into retene, $C_{18}H_{18}$ (E. and B., *l.c.*; Vesterberg, Ber. 1903, 4200). Oxidation with potassium permanganate yields an acid $C_{16}H_{16}O_3$, m.p. 123° (Mach, Monatsh. 1894, 627); and a method has been devised by Endemann (D. R. P. 183328; Chem. Zentr. 1907, i. 1607) to oxidise resinous materials, containing abietic acid, to resin acids and malonic acid.

Abietic acid is related to retene and pinene, contains a *cyclo*-hexane ring and an *iso*-propyl group, and has its carboxyl group attached to a tertiary carbon atom (Levy, Zeitsch. anorg. Chem. 1913, 81, 145).

Sodium and *potassium* abietates are prepared by direct neutralisation; the *silver* (white), *copper* (pale blue), *calcium, barium, strontium, cobalt* (lavender), *nickel* (greenish-yellow), *iron* (light brown), *zinc, chromium* (greenish-yellow), *aluminium, manganese* (pale pink), and *cadmium* salts are obtained by precipitation of solutions of salts of the respective metals by a solution of the alkaline abietate (Ellingson, *l.c.*).

It is converted by the hydrogenation method of Willstatter and Hatt into hydroabietic acid $C_{19}H_{32}O_2$, m.p. 176°–179°, $[\alpha]_D^{16} -16·85°$, identical with the acid obtained by Maly by reduction with sodium amalgam and alcohol. For the optical isomerism of the abietic acids, *see* Schulz, Chem. Zeit. 1917, 41, 666.

Detection and Estimation.—The following colour reactions may be used for detecting abietic acid:—(1) 3 vols. of conc. hydrochloric acid and 1 vol. of ferric chloride sol. give a violet red colouration; (2) sulphuric acid dissolves abietic acid to a red solution; (3) when heated with dry chloroform, acetic anhydride and sulphuric acid, a purple red colour is produced changing through violet and blue to a greenish black (Mach. *l.c.*). In order to estimate abietic acid in resins, &c., 10 grms. of the substance are refluxed with 20–25 c.c. of 10 p.c. alcoholic potash for ½ hour on a water-bath; the resulting soap is decomposed with dilute hydrochloric acid, and the separated resin filtered off, washed with cold water and dried. It is then powdered and extracted with 50 c.c. of hot petroleum ether. From this solution abietic acid is precipitated by ammonia, filtered off, dried on the water-bath, and the ammonia expelled by gentle heating. The residue represents the amount of crude abietic acid in the sample (Rebs, Chem. Zentr. 1907, i. 997).

Abietic acid (or colophony) is used in assisting the growth of lactic or butyric ferments, as it favours the production of that which is present in the greater quantity and suppresses the other. It promises to be of great use in the fermentation industry in preventing infection (Effront, Compt. rend. 136, 1556), (*v.* COLOPHONY).

ABISOL. Trade name for a 40 p.c. solution of sodium bisulphite. Used as a disinfectant and preservative.

ABRASIVES. The various hard substances, chiefly of mineral origin, used for abrasive purposes fall naturally into the following groups, in which the hardness is roughly inversely proportional to the complexity of chemical composition.

Elements.—Diamond (*q.v.*) is the hardest of all substances (hardness = 10 on Mohs's scale). Inferior material of no use for gems is known as boart (or bort), and is crushed to powder and much used by lapidaries. Diamond powder is the only material with which diamond itself can be ground and polished. Embedded in the edge of a thin disc of soft iron, diamond powder is largely used for cutting gem-stones and thin sections of rock specimens, and also for slicing larger blocks of the harder ornamental stones. A black, compact variety of diamond known as carbonado ('carbonate' or 'carbon') is embedded in the steel crowns of rock-drills.

Amongst artificial products, steel and some other hard metals are used for abrasive purposes. The so-called crushed steel, made by quenching white-hot crucible steel, is used in the stone-cutting trade. Tantalum is an extremely hard metal and may in future find some application depending on hardness.

Carbides.—Carborundum[1] (*q.v.*) or silicon carbide, CSi (H.=9½), is prepared artificially in the electric furnace from petroleum-coke and the purest quartz-sand, and is produced in large quantities at Niagara Falls. It is largely made into sharpening stones and grinding wheels; and sold under a variety of trade-names, *e.g.* crystolon, exolon, samite, &c. In lapidaries' work it has to a large extent taken the place of corundum; but although harder than corundum, it has the disadvantage of being more brittle, and it soon rubs to flour. Carbide of boron, CB_6, and silicide of boron, SiB_3, are also remarkable on account of their intense hardness (H. Moissan, Compt. rend. 1894, cxviii, 556).

Oxides.—Corundum (*q.v.*) Al_2O_3 is, next to diamond, the hardest of minerals (H. = 9). The impure variety, emery (*q.v.*), is not quite so hard. The crushed and graded material is made into corundum wheels and emery paper, and is much used in lapidaries' work. Artificial corundum, known by the trade-names of 'alundum,' 'aloxite,' 'adamite,' 'borocarbone,' &c., is now manufactured in considerable amounts at Niagara Falls, by fusing bauxite in an electric furnace. 'Corubin' is also an artificial corundum, formed as a by-product in the Goldschmidt thermite process.

Quartz (*q.v.*) SiO_2 (H. = 7), and its several varieties find extensive applications. Millstones and grindstones are made of quartz-rock, quartzite, burrstone (or buhrstone), grit, or sandstone (*q.v.*); while scythe-stones, oilstones and whetstones (*q.v.*) consist of hornstone, lydian-stone and other compact varieties of quartz. In the form of sand, quartz is used as a sand-blast, in scouring-soap, for cutting and grinding marble, making sand-paper, &c. Tripoli or infusorial earth is a powdery variety of opal (hydrated silica), and is used for polishing.

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[1] So named by E. G. Acheson, in 1893, from carbon and corundum, because before it had been analysed, it was thought to be a compound of carbon and alumina

Silicates.—Garnet (*q.v.*) (H. = 6½–7½) is used for making 'emery' paper and cloth; and felspar (*q.v.*) (H.=6) is also used to a small degree. Silicate rocks are employed to a small extent; *e.g.* pumice for polishing, and the millstone lava (leucite-nepheline-tephrite) of Niedermendig on the Rhine, for millstones.

References.—J. V. Lewis, Abrasives (Mineral Industry, New York, 1916, 1917, xxv, 22–33); F. J. Katz, Abrasive Materials (Mineral Resources of the United States, U.S. Geol. Survey, 1915, 1916, ii, 65–80); H. Ries, Economic Geology (New York, 1916, 284-297, with bibliography).

L. J. S.

ABRASTOL or *Asaprol - Etrasol.* Trade names for the calcium salt of β-naphthol-sulphonic acid, $Ca(C_{10}H_7OSO_3)_2,3H_2O$, used in the clarification and preservation of wines. The maximum quantity needed for this purpose is 10 grms. per hectolitre. According to Noelting and Dujardin-Beaumetz and Stackler, the substance is harmless from a hygienic point of view (see Mon. Sci. 1894, 8, 257; J. Soc. Chem. Ind. 1894, 177, 534). To detect its presence, Sanglé-Ferrière proceeds as follows (Compt. rend. 1893, 117, 796): 200 c.c. of the wine is boiled for an hour in a reflux apparatus with 8 c.c. of hydrochloric acid, when the abrastol is hydrolysed to β-naphthol, which may be extracted with benzene, and the residue left after distilling the benzene sol. taken up with chloroform. A fragment of potash is dropped into the chloroform solution, which is boiled for 2 mins., when a blue colouration is produced changing to green and finally becoming yellow. 0·1 grm. per litre may thus be detected. The presence of abrastol in no way vitiates the determination of potassium sulphate (J. Soc. Chem. Ind. 1894, 177). Sinibaldi (Mon. Sci. 7, 842) has given the following method: 25 c.c. of the wine are neutralised by ammonia and shaken with 25 c.c. of amyl alcohol. After separation, the amyl alcohol is boiled to expel ammonia, and when cold is shaken with 0·25 c.c. ferric chloride sol. A grey-blue colouration denotes abrastol. Gabutti (Chem. Zentr. 1904, 2, 370) proceeds in a similar way, but instead of ferric chloride, employs phosphoric acid and formaldehyde solution, when, in presence of abrastol, a green fluorescence is produced. (For other methods, *v.* Sanna Pintus, J. Soc. Chem. Ind. 1900, 933; Briand, Compt. rend. 1894, 118, 925; Carletti, Chem. Zentr. 1909, 2, 72. For colour reactions, *v.* Barral, J. Pharm. Chim. 1903, 18, [5] 206; Salomone, Chem. Zentr. 1907, i. 306.) (For a review of the various methods of detection, *v.* Vitali, Apoth. Zeit. 1908, 23, 507; J. Soc. Chem. Ind. 1908, 830.)

ABRAUM SALTS. (Ger. *Abraumsalze*: 'salts to be removed.') The mixed salts found overlaying the rock-salt deposit at Stassfurt, in Prussia. These consist mainly of rock salt; *Carnallite*, a double chloride of potassium and magnesium; *Sylvine*, or potassium chloride; and *Kieserite*, or magnesium sulphate, *v.* POTASSIUM.

ABRIN. A brownish yellow soluble substance obtained from the seeds of *Abrus precatorius* (*Indian liquorice* or *Jequirity*). Contains a poisonous proteid, resembling, if not identical with, ricin. Lethal dose, according to Kobert, is only 0·00001 grm. per kilo body-weight: *i.e.* 1 to 100,000,000.

ABROTINE $C_{21}H_{22}ON_2$ is a crystalline diacid fluorescent alkaloid from *Artemisia abrotanum*, somewhat resembling quinine (Giacosa, Jahresber. 1883, 1356).

ABSINTH. (*Absinthe*, Fr.; *Wermuthextract*, Ger.) One of the best-known liqueurs or cordials (*q.v.*), is made chiefly at Lyons, Montpellier and Pontarlier in France, and in former years (*vide infra*) at Neufchâtel in Switzerland. It is a highly intoxicating spirituous liquor flavoured with oil of wormwood (*Artemisia absinthium*, nat. ord. *Compositæ*) and other essential oils as angelica, anise, cinnamon, cloves, fennel, hyssop, peppermint, &c. (*v.* OILS, ESSENTIAL).

There are three distinct processes in the manufacture of absinth, viz.: maceration, distillation, and colouration. The leaves and flower-tops of *Artemisia absinthium*, together with the other flavouring ingredients (which vary in kind and quality according to the requirements of the different manufacturers) are digested with spirit for periods varying from 12 hours to 10 days, according to the temperature of the infusion and the strength of the spirit used. The French manufacturers, as a rule, digest for short periods at the temperature of an ordinary water bath, and with spirit containing about 85° alcohol, whilst the Swiss maceration process was conducted at air temperature with spirit somewhat below British 'proof' strength, or about 50° alcohol.

The infusion is distilled and the distillate transferred to the colouring vessel containing small absinth leaves, balm and hyssop, dried and finely divided. This vessel is hermetically sealed and is gently heated by steam to a temperature of 60° in order to extract chlorophyll. After cooling, the green liquor is drawn off, and strained, if necessary, through a hair sieve. The colouring is sometimes separately prepared and added as required to the colourless distillate. Occasionally the latter is sweetened by the addition of about 5 p.c. by weight of crushed white sugar. Chlorophyll for imparting the green colour to absinth (and other liqueurs) is frequently obtained from nettles, parsley, and spinach, and is free from objection provided the vegetable matter is sound.

On keeping, genuine absinth assumes the yellowish tint appreciated by connoisseurs, and its qualities generally are improved by age. Many objectionable varieties of absinth are, however, on the market, made from inferior spirit, to which essences and resins are added, the former to give a fictitious flavour and the latter to produce the opalescence which occurs in genuine absinth on the addition of water, owing to the liberation of the essential oils, resinous bodies, and colouring matters derived from the plants and seeds used in its manufacture. Other colouring matters than chlorophyll are also employed, as indigo, sulphate of copper, picric acid and turmeric or other vegetable colour. Gum benzoin, guiacum and rosin are also used to produce 'milkiness' on dilution, and even chloride of antimony is said to have been employed for this purpose.

To detect adulteration it is usually sufficient to determine the essential oils, resins, and colouring matters (*vide* Hubert, Ann. Chim. anal. 6, 409, and Nivière and Hubert, Mon. Sci. 1895, 566). According to Hubert, absinth has a specific gravity of 0·8966 to 0·9982, and alcoholic strength of 47 to 72 p.c. by volume of absolute alcohol. The average results of twelve samples expressed as grams per litre were as follows: essential oils, 1·5 to 5·0; extractive, 0·36 to 1·72; acids, 0·024 to 0·288; aldehydes, 0·005 to 0·155; furfurol, 0·0002 to 0·007; ethers, 0·005 to 0·123. The strength of absinth as imported into the United kingdom varied from 'proof' to about 20 over proof, and rather more than 3000 gallons were imported annually before the war. The amount rose to 4000 gallons in 1915, since when its importation into the United Kingdom has been prohibited.

Although genuine absinth, taken in moderation, has valuable qualities as a cordial, stomachic, and febrifuge, its characteristic bitter principle, absinthiin (*q.v.*), is an active poison, having a very injurious effect upon the nervous system of those addicted to the habitual and immoderate consumption of absinth. Legal measures have therefore been taken in various European countries to control, restrict, or even prohibit its sale. In France, liqueurs may not contain more than 1 gram per litre of oil of wormwood or other oil of similar toxic nature, whilst in Belgium and Swizerland the manufacture and sale of absinth have been entirely prohibited. J. C.

ABSINTHIN or **ABSINTHIIN** $C_{15}H_{20}O_4$. The bitter principle extracted from the dried leaves of large absinth or wormwood (*Artemisia absinthium*) is an active poison. and it is to its presence in oil of wormwood that the toxic effect of absinth (*q.v.*) appears to be due.

Various formulæ have been assigned to this substance, the differences being due to the difficulty of obtaining it in a pure state (Mein, Annalen, 8, 61; Luck, Annalen, 78, 87; Kromayer, Arch. Pharm. [2] 108, 129).

Pure crystallised absinthiin was first isolated by Duquesnel (Bul. de Therapeutique, 107, 438). Senger obtained absinthiin as a pale yellow amorphous substance melting at 65° and having the empirical formula $C_{15}H_{20}O_4$. This formula was confirmed later by Bourcet, who found that the pure substance crystallises in fine white prismatic needles melting at 68°, the amorphous form and lower melting-point found by Senger being probably due to traces of a resinous impurity.

According to Senger and Bourcet, absinthiin is a glucoside, free from nitrogen, and is decomposed by the action of dilute acids, or even by boiling with water, into dextrose, a volatile oil, and a solid resinous body of the aromatic series. It is soluble in alcohol, ether, chloroform, or benzene; difficultly soluble in light petroleum, water, though more soluble in cold than in boiling water. It gives a precipitate with tannic acid and with gold chloride, which is reduced on warming; yields volatile fatty acids on oxidation with nitric acid, and oxalic and picric acids with potassium chromate and sulphuric acid. With Fröhde's reagent it gives a brown colour, changing to violet, then blue; and with sulphuric acid brown, passing through green to blue (Senger, Arch. Pharm. 230, 103; and Bourcet, Bull. Soc. chim. [3] 19, 537). J. C.

ABSINTHOL $C_{10}H_{16}O$. The essential principle of oil of wormwood derived from *Artemisia absinthium* (nat. ord. *Compositæ*), a plant indigenous to most European countries and comparatively recently introduced into the United States of America, whence increasing supplies of the cheaper qualities of wormwood oil are now obtained.

Although the oil obtained by the distillation of wormwood has been known for at least four centuries, its chemical composition was first systematically investigated in 1845, when Leblanc (Compt. rend. 21, 379) showed that its principal constituent, boiling at 203°, has the formula $C_{10}H_{16}O$. This was confirmed later by Gladstone and other investigators (Chem. Soc. Trans. 17, 1), and by Beilstein and Kupffer (Annalen, '70, 290), who gave to the product the name '*absinthol*,' and identified its dehydration product with *cymene*.

Methods for the identification of absinthol have been described by Cuniasse (J. Pharm. Chim. 1907, 25 (180–2)) and Enz (Chem. Zentr. 1911, ii. 576), but these can hardly be accepted as conclusive of the presence of wormwood, since thujone occurs in other plants. A negative reaction, however, proves the absence of wormwood.

Semmler (Ber. 25, 3350) proved absinthol to be a ketone identical with thujone or tanacetone, which occurs largely in other essential oils, as oil of tansy, sage, and *Artemisia barelieri*. It is a colourless oily liquid of pleasant odour, strongly dextrorotatory (about +68°), boils at 203°, density 0·9126 at 20°, and refractive index 1·4495.

Though isomeric with camphor, it differs from that body in combining with sodium bisulphite and in not being converted into camphoric acid by means of nitric acid, nor into camphocarboxylic acid by treatment with carbon dioxide and sodium. With melted potash it gives a resin, but no acid. When heated with P_2S_5 and $ZnCl_2$ it yields cymene (Beilstein and Kupffer, Ber. 6, 1183; Annalen, 170, 290; Wright, Chem. Soc. Trans. 27, 1 and 319; Semmler, Ber. 25, 3343 and 27, 895). J. C.

ABUTILON INDICUM (Sweet), **PETAREE** or **TUBOCUTY.** The bark of this malvaceous tree consists of long, thin, tough fibrous strips (bast fibres), and, according to Dymock (Pharm. J. [3] 8, 383) and others, is worthy of attention as a source of fibre.

ABYSSINIAN GOLD. A yellow alloy of 90·7 parts of copper and 8·3 of zinc. The ingot is plated on one side with gold, and is then rolled out into sheets, from which articles of jewellery are formed in the usual way, the amount of gold on the finished article varying from 0·03 to 1·03 p.c. Known also as *Talmi gold*. The term is sometimes applied in trade to Aluminium Bronze.

ACACIA BARK. *Acaciæ Cortex*, B. P. The dried bark of *Acacia arabica* (Willd) and of *A. decurrens* (Willd).

ACACIA CATECHU (Willd) or **KHAIR** is a tree growing in various parts of India. Its unripe pods and wood, by decoction, yield a catechu (Agricult. Ledger, 1895, No. 1, and 1896, No. 25), known by the name of Cutch or Kutch, which must not be confounded with the officinal catechu (*Catechu pallidum*). It is used in the preparation of some leather and by dyers. The timber is also used for constructional and other purposes.

ACACIA GUM *v.* Gums.

ACANTHITE. A form of silver sulphide found at the Enterprise mine, near Rico, in black crystals of orthorhombic habit (Chester, Zeitsch. Kryst. Min. 1896, 26, 526)

ACAROID RESIN or **BOTANY BAY RESIN** *v. Xanthorrhœa Balsams*, art. Balsams.

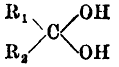
ACCIPENSERINE. A protamine belonging to the sturine group found in the testis of *Accipenser stellatus.* Composition of the sulphate: $C_{35}H_{72}O_9N_{18},4H_2SO_4$ (Kuraéeff, Zeitsch. physiol. Chem. 1901, 32, 197).

ACENAPHTHENE QUINONE. *See* Quinones.

ACERDOL. Trade-name for calcium permanganate.

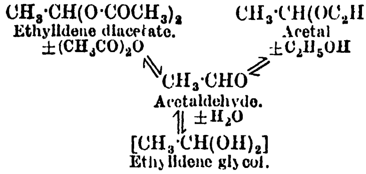
ACETAL (diethyl acetal; ethylidene diethyl ether; ethanediol (1 : 1) diethyl ether) $C_6H_{14}O_2$, or $CH_3{\cdot}CH(OC_2H_5)_2$. *See* Acetals.

ACETALS. Acetals are the ethers and esters derived from the so-called *geminal*-glycols, which are themselves for the most part incapable of existence; such glycols possess the general formulæ—

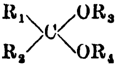


$$R_1R_2C(OH)_2$$

(where R_1 and R_2 may be either hydrogen or aliphatic or aromatic radicals); they split up at once into water and the corresponding anhydrous compound, which may be an aldehyde or a ketone; thus, in the case of ordinary acetaldehyde, we have the relationships:



Acetals may thus be given the general formula:



$$R_1R_2C(OR_3)(OR_4)$$

(where R_1 and R_2 are any alkyl or aryl radicals, and R_3 and R_4 any acidyl, alkyl or aralkyl radicals).

We may distinguish two types of acetals, according to whether the products are alkyl ethers or acid esters; the term '*acetal*' is more usually applied to the former class.

(*a*) *Dialkyl Ethers of* gem.-*Glycols* (Acetals of Aldehydes and Ketones).

They are produced by heating alcohol and an aldehyde alone, but the yield is very poor (Geuther, Annalen, 126, 62). A better yield is obtained by adding a small quantity of a catalyst such as ferric chloride, or a trace of acid to the mixture (Trillat and Cambier, Compt. rend. 118, 1277). Still better is the method of Fischer and Giebe (Ber. 30, 3053; 31, 545), consisting in passing 1 p.c. of hydrochloric acid into the mixture and heating, or allowing to stand for some time; after washing with a little dilute potassium carbonate solution the product is dried over anhydrous potassium carbonate and fractionated, the yield, however, is only about 50 p.c. in the case of diethyl acetal, as the reaction is reversible:

$$R{\cdot}CHO+2C_2H_5{\cdot}OH \rightleftharpoons R{\cdot}CH(OC_2H_5)_2+H_2O$$

Acetals may also be made by passing pure phosphine through the cooled mixture of aldehyde and alcohol (Girard, Compt. rend. 91, 629).

The most convenient method for the preparation of acetals is, perhaps, that described by King and Mason (Eng. Pat. 101428), consisting in treating a mixture of an aldehyde and an alcohol with certain metallic salts—or their saturated aqueous solutions—such as the chlorides or nitrates of aluminium, calcium, cerium, magnesium, manganese, &c., thus 50 grams acetaldehyde and 120 grams 95 p.c. alcohol are mixed and then 20 grams anhydrous calcium chloride are added. The mixture becomes warm, and is allowed to stand for some time, with occasional shaking. It has then separated into two layers, the upper of which is removed, washed with water, then with sodium carbonate solution, dried over calcium chloride, and finally over anhydrous potassium carbonate. It is then fractionated, and yields 120 grams acetal, or 90 p.c. of theory. The addition of a small quantity of an acid has the effect of causing the reaction to take place more quickly.

It is also possible to prepare certain acetals by heating another acetal with the desired alcohol:

$$R{\cdot}CH(OR_1)_2+2R_2{\cdot}OH \rightleftharpoons R{\cdot}CH(OR_2)_2+2R_1{\cdot}OH$$

Thus on heating ordinary diethyl acetal with excess of methyl alcohol it is converted almost completely into dimethyl acetal (Delépine, Compt. rend. 132, 968; Bull. Soc. chim. [3], 25, 574). The converse, however, does not hold good, since, on heating dimethyl acetal with excess of ethyl alcohol practically no reaction occurs (Geuther and Bachmann, Annalen, 218, 44). In general, the series of acetals can be descended by heating any member of the group with an alcohol containing a smaller number of carbon atoms than is present in its alcohol residue. If a little hydrochloric acid be added a balanced reaction takes place, and a certain proportion of all the possible products is obtained, the products of higher molecular weight predominating (Delépine, Compt. rend. 132, 331, 968). Another general method of wide applicability is that of Claisen (Ber. 29, 1007; 31, 1010; 40, 3903), consisting in treating the aldehyde or ketone with orthoformic ester in alcoholic solution in presence of a suitable catalyst, such as mineral acids, oxalic acid, ferric chloride, ammonium chloride, sulphate or nitrate, &c. (*cf.* also Arbusow, Ber. 40, 3301; Claisen, *ibid.* 40, 3912). Orthoformic esters can also react with alkylmagnesium salts to yield acetals (Bodroux, Compt. rend. 138, 700; Tschitschibabin, Ber. 37, 186), or with halogenated fatty esters in presence of zinc (Tschitschibabin, J. prak. Chem. [2] 72, 326; Claisen, Ber. 31, 1019):

$$(C_2H_5O)_2{\cdot}CH{\cdot}OC_2H_5+Br{\cdot}CH(CH_3){\cdot}COOR+Zn$$
$$=(C_2H_5O)_2{\cdot}CH{\cdot}CH(CH_3){\cdot}COOR+C_2H_5O{\cdot}ZnBr$$
$$(C_2H_5O)_2{\cdot}CH{\cdot}CH(CH_3){\cdot}COOR$$
$$\rightarrow (C_2H_5O)_2{\cdot}CH{\cdot}CH(CH_3){\cdot}COOH$$
$$\rightarrow (C_2H_5O)_2{\cdot}CH{\cdot}CH_2{\cdot}CH_3$$

Certain special methods for production of acetals are available for formylal and diethyl acetal, and will be noted later.

General Properties.—The true acetals, or dialkyl ethers of *gem*-glycols, are colourless liquids of pleasant ethereal odour, which can be distilled without decomposition. The lower members are somewhat soluble in water, by which they are slowly hydrolysed; in presence of dilute acids the hydrolysis is almost instantaneous; they are stable to alkalis even on boiling. With various metallic salts such as magnesium or zinc iodides, calcium chloride or magnesium bromide, double compounds are formed, *e.g.* $MgBr_2+2CH_2(COCH_3)_2$, m.p. 112°; $MgI_2+2CH_3{\cdot}CH(OC_2H_5)_2$, m.p. 86° (Timmermans, Chem. Zentr. 1907, 1, 1007). The acetals form hydrates in certain cases; thus, diethyl formylal forms a hydrate $CH_2(OC_2H_5)_2{\cdot}H_2O$, which is a liquid of b.p. 74°–75°, with an odour of rum, and dissolves in 15 parts water at 20° C.; the higher homologues also form monohydrates, boiling at lower temperatures than the acetals themselves (Trillat and Cambier, Compt. rend. 118, 1278).

The acetals are of considerable use in place of the free aldehydes or ketones for synthetic purposes, on the one hand, owing to their higher boiling-points (*e.g.* acetaldehyde, b.p. 20°; diethyl acetal, b.p. 103°), and also to the fact that alcohol and not water is split off in the condensation, which has a marked effect on the yield. Thus in preparing vinyldiacetoneamine by condensing acetaldehyde or paraldehyde with diacetoneamine acid oxalate (Fischer, Ber. 17, 1793; Heintz, Annalen, 178, 326; 191, 122; Harries, Ber. 29, 522), only a poor yield of product is obtained even on prolonged heating: but if acetal be substituted the reaction is complete in a few hours with almost quantitative yield (*cf.* King, Mason and Schryver, Eng. Pat. 101738) owing probably to the absence of the inhibiting effect of water.

In addition, the acetals can be readily halogenated and converted into amino-, hydroxy-, alkoxy-, &c., derivatives, which react like the corresponding aldehydes.

They can be separated from their aqueous solutions by the addition of concentrated calcium chloride solution. They are miscible with alcohol and ether; their vapours or solutions in alcohol, benzene, or acetone slowly harden dry gelatine films (Beckmann and Scharfenberger, Chem. Zentr. 1896, ii. 930). When heated in a sealed tube with glacial acetic acid the corresponding aldehyde is obtained (Beilstein, Annalen, 112, 239).

Mixed acetals containing two different alcohol residues have been described by Bachmann (*l.c.*), but according to Rübencamp (Annalen, 225, 271) and Fritz and Schumacher (Annalen, 279, 308), these consist of mixtures of two acetals in molecular proportions. Delepine, however (Compt. rend. 132, 331, 968), claims to have obtained mixed acetals.

Formylals $CH_2{\cdot}(OR)_2$.

Methylal $CH_2{\cdot}(OCH_3)_2$ (dimethyl formylal), b.p. 41·3–41·7°, sp. gr. 0·862, can be obtained by treating a mixture of methyl alcohol and 40 p.c. formaldehyde solution, with solid calcium chloride and a little hydrochloric acid (Fischer and Giebe, Ber. 30, 3054). It can also be obtained by treating methylene chloride with sodium methylate (Arnhold, Annalen, 240, 197), and also by treating chlormethyl alkyl ether $CH_2(OR)Cl$ (obtained by condensing formaldehyde and alcohol with excess of hydrochloric acid) with sodium methylate (Favre, Compt. rend. 119, 284; Bull. Soc. chim. [3] 11, 879; Henry, Ber. 26, Ref. 933; Compt. rend. 119, 425; de Sonay, Ber. 27, Ref. 337); or by heating polyoxymethylene and the required alcohol with 1 to 4 p.c. ferric chloride for 2–10 hours (Trillat and Cambier, Compt. rend. 118, 1277). It can be used for various condensations in place of formaldehyde, and is a good solvent for many organic compounds. (*Cf.* also Kane, Annalen, 19, 175; Malaguti, Annalen, 32, 55; Renard, Ann. chim. phys. [5] 17, 290; Brühl, Annalen, 203, 12, 25; Fileti and de Gaspari, Gazz. chim. Ital. 27, ii. 293; Trillat, Compt. rend. 137, 187; Delépine, Bull. Soc. chim. [3] 25, 364; Favre, Bull. Soc. chim. [3] 11, 1096; Brühl, Ber. 30, 159; Berthelot, Compt. rend. 126, 675; Trillat and Cambier, Compt. rend. 118, 1277; Brochet, Bull. Soc. chim. [3] 13, 687.)

The following formylals are known, but the higher members are of little importance:—

Diethyl methylal $CH_2{\cdot}(OC_2H_5)_2$, b.p. 87°; sp. gr. 0·834 (20°) (Arnhold, *l.c.*; Greene, Chem. News, 50, 75; Pratesi, Ber. 16, 1870; Favre, *l.c.*; Trillat and Cambier, Compt. rend. 118, 1278).

Dipropyl methylal $CH_2{\cdot}(OC_3H_7)_2$, b.p. 136°; sp. gr. 0·834 (20°) (Arnhold, *l.c.*; Trillat and Cambier, *l.c.*; Favre, Bull. Soc. chim. [3] 11, 881).

Di-isopropyl methylal $CH_2(OC_3H_7)_2$, b.p. 118°; sp. gr. 0·831 (20°) (Arnhold, *l.c.*; Trillat and Cambier, *l.c.*).

Di-isobutyl methylal $CH_2(OC_4H_9)_2$, b.p. 164°; sp. gr. 0·824 (20°) (Arnhold, *l.c.*; Gorbow and Kessler, Ber. 20, Ref. 778; Trillat and Cambier, *l.c.*).

Di-isoamyl methylal $CH_2(OC_5H_{11})_2$, b.p. 206°; sp. gr. 0·835 (20°) (Arnhold, *l.c.*; Trillat and Cambier, *l.c.*).

Dihexyl methylal $CH_2(OC_6H_{13})_2+H_2O$, b.p. 174°–175°; sp. gr. 0·822 (15°) (Trillat and Cambier, *l.c.*).

Dioctyl methylal $CH_2{\cdot}(OC_8H_{17})_2$, b.p. 280°; sp. gr. 0·848 (15°) (Arnhold, *l.c.*; Trillat and Cambier, *l.c.*).

Cyclohexanol formal $(C_6H_{11}O)_2{\cdot}CH_2$ is produced from cyclohexanol, 40 p.c. formaldehyde solution and hydrochloric acid (Murat and Cathala, J. Pharm. Chim. 6, 289).

Acetals $CH_3{\cdot}CH(OR)_2$.

Dimethyl acetal $CH_3{\cdot}CH(OCH_3)_2$ occurs in crude wood-spirit, b.p. 63°; sp. gr. 0·865 (22°) (Dancer, Annalen, 132, 240; Alsberg, Jahresb. f. Chem. 1864, 485; Geuther and Bachmann, Annalen, 218, 44; Schiff, Annalen, 220, 104; 223, 74).

Diethyl acetal $CH_3{\cdot}CH(OC_2H_5)_2$ (usually known simply as 'Acetal') (= ethylidene diethyl ether; ethane-diol-(1 : 1)-diethyl ether) (*cf.* Döbereiner, Gm. 4. 805; Liebig, Annalen, 5, 25; 14. 156; Stas. Ann, Chim. Phys. [3] 19, 146; Wurtz, Ann. Chim. Phys. [3] 48, 70; Geuther, Annalen, 126, 63).

To prepare acetal by Wurtz's method, 2 parts alcohol are added to a mixture of 3 parts manganese dioxide, 3 parts sulphuric acid and 2 parts water, and, after the effervescence first produced has subsided, the whole is heated at 100° until 3 parts have distilled over. The product is then fractionally distilled, and two portions, one boiling below 80° and the second boiling at 80°–95°, are collected.[1] Each fraction is treated with solution of calcium chloride and the ethereal layer which separates is distilled. The product contains aldehyde and ethyl acetate in addition to acetal; to remove these it is shaken with concentrated aqueous potash, the brown liquid separated from the aqueous layer is distilled, and the distillate shaken with calcium chloride. It is then heated with twice its volume of concentrated aqueous soda in sealed tubes at 100° for 24 hours, separated from the soda, distilled, the distillate again rectified: the fraction 100°–105°, which constitutes the greater portion, is acetal.

In addition to its formation as a by-product in the oxidation of alcohol, acetal can also be obtained from a mixture of acetaldehyde (1 vol.) and absolute alcohol (2 vols.) (1) by heating with acetic acid (½ vol.) for 12 hours at 100° (Geuther, Annalen, 126, 63); (2) by cooling in a freezing mixture, passing dry hydrogen chloride to saturation, and decomposing the resulting monochlorether with sodium ethoxide (Wurtz and Frapolli, Compt. rend. 67, 418; Annalen, 108, 223); or (3) by cooling a mixture of equal volumes to −21°, and passing a current of pure hydrogen phosphide for 24 hours (Engel and Girard, Compt. rend. 92, 692; J. 1880, 694).

The most convenient method is that of King and Mason (E. P. 101428, *vide supra*). On a technical scale considerable interest attaches to the production of diethyl acetal from acetylene by a modification of the process of Kutscherow for preparing acetaldehyde from acetylene and water in the presence of a mercury catalyst (*cf.* Kutscherow, Ber. 14, 1540; 42, 2759). Thus the Chemische Fab. Griesheim Elektron (E. P. 14246, 1913) describe the production of ethers of ethylidene glycol by the action of acetylene upon alcohols in the presence of mercury salts. They are stated to be solvents for cellulose esters. Boiteau (E. P. 15806, 1914) describes the production of ethylidene ethers by a similar method; and in E. P. 15919, 1914, a further modification is claimed, consisting in forming the catalyst *in situ*, *e.g.* by adding mercuric oxide or the mercury salt of a weak acid to the liquid, and then adding sulphuric acid to form the sulphate.

Acetal is a colourless liquid with agreeable odour: b.p. 104°, and sp. gr. 0·821 at 22·4° (Stas, Annalen, 64, 322); b.p. 103·7°–104·3° at 744·4 mm., and sp. gr. 0·8314 at 20°/4° (Brühl, Annalen, 203, 25). It is soluble in 18 vols. of water at 25°, and the solubility increases as the temperature rises. Acetal is miscible in all proportions with alcohol and ether, does not reduce ammoniacal silver solution, and is unaltered on exposure to air; platinum black, however, oxidises it first to acetaldehyde and subsequently to acetic acid. For formation and hydrolysis, *see* Lapworth and Fitzgerald (Proc. Chem. Soc. 24, 153).

Acetal has some solvent power for cellulose esters. A use for acetal is suggested by Ostromisslensky, consisting in preparing erythrene (butadiene) from it by passing over a heated catalyst, such as alumina at 360°–460° (J. Russ. Phys. Chem. Soc. 47, 1472, 1509; *cf.* also Boiteau, E. P. 15806, 1914). Pictet (Ber. 46, 2688; E. P. 17578, 1914) describes the production of a synthetic alkaloid, which he terms *coralydine*, by condensing tetrahydropapaverine and acetal in 16 p.c. hydrochloric acid on the water-bath; the product exists in two isomeric forms, α- and β-.

On heating with phosphorus pentoxide the elements of alcohol are removed from acetal, leaving vinyl ethyl ether:

$$CH_3{\cdot}CH(OC_2H_5)_2 - C_2H_5OH = CH_2{:}CH{\cdot}O{\cdot}C_2H_5$$

which forms a liquid, b.p. 35·5°; sp. gr. 0·762 (14·5°), and is split up by dilute sulphuric acid into acetaldehyde and alcohol (Wislicenus, Annalen, 192, 106; Henry, Compt. rend. 100, 1007; Nef. Annalen, 298, 327; Claisen, Ber. 31, 1021; Tschitschibabin, J. prak. Chem. [2] 74, 424). When heated with acetic anhydride to 150° one ethyl group is replaced by an acetyl group yielding 'acetaldehyde-ethyl acetate,' $CH_3{\cdot}CH(O{\cdot}C_2H_5)(O{\cdot}CO{\cdot}CH_3)$, b.p. 125°–130°; sp. gr. 0·941. On boiling with water it splits up into acetaldehyde, ethyl alcohol, and acetic acid (Claisen, Ber. 31, 1018).

Acetal does not give the iodoform reaction until shaken with a few drops of hydrochloric acid, whereby the acetal is hydrolysed to alcohol and aldehyde. Estimation in presence of paraldehyde, see Orton and McKie, Trans. Chem. Soc. 109, 184.

Derivatives.—Mono-, di-, and trichloracetal are obtained as intermediate products in the preparation of chloral by passing chlorine through 80 p.c. alcohol (Lieben, Ann. Chim. Phys. [3] 52, 313; Paternò, Compt. rend. 67, 765). According to Krey (J. 1876, 475), a better yield of these derivatives is obtained if a mixture of 2 parts absolute alcohol, 3 parts manganese dioxide, 3 parts sulphuric acid, and 2 parts water is heated until ⅔ of the liquid has distilled over and chlorine is passed through the well-cooled distillate until it shows signs of turbidity. In either case the product is washed with water, dried over calcium chloride, and submitted to fractional distillation. The fraction 80°–120° contains chiefly aldehyde and compound ethers, 120°–170° chiefly monochloracetal, 170°–185° dichloracetal (Lieben, *l.c.*), and the fraction boiling above 185° contains trichloracetal (Paternò, *l.c.*). These compounds may then be obtained in the pure state by repeated fractionation.

A better method of obtaining monochloracetal is by passing chlorine through well-cooled 94–99 p.c. alcohol until the chlorinated product has a sp. gr. 1·02–1·03 at 25°. Half the original volume of alcohol is added and the mixture heated a few hours at 50°–60°. The free acid is removed by calcium carbonate; the oil washed with water, dried and fractionated. The proportion of di- and tri- chloro-derivatives formed depends on the amount of chlorine added (Fritsch, Annalen, 279, 288).

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[1] The b.p. is given as in the original paper, but, inasmuch as b.p. of acetal is 104°, it seems probable that 95° is a misprint for some higher temperature—say 105°.

Monochloracetal $CH_2Cl\cdot CH(OC_2H_5)_2$ (Lieben, Annalen, 146, 193; Paternò, Mazzara, Ber. 6, 1202; Klien, J. 1876, 336; Natterer, Monatsh. 3, 444; 5, 497; Wislicenus, Annalen, 192, 106; Frank, Annalen, 206, 341; Fritsch, Annalen, 279, 300) is a colourless liquid, having an aromatic ethereal odour; b.p. 155°; sp. gr. 1·0418 at 0°, 1·026 at 15° (Klien): 156°–158° (Autenrieth, Ber. 24, 159). When heated with bleaching powder it yields di- and trichloracetal, chloroform, and chlorinated acetaldehyde (Goldberg, J. pr. Chem. [2] 24, 107).

Dichloracetal $CHCl_2\cdot CH(OC_2H_5)_2$ (Jacobsen, Ber. 4, 217; Pinner, Ber. 5, 148; Annalen, 179, 34; Krey, *l.c.*; Paternò, Annalen, 149, 372; 150, 134); b.p. 183°–184°; sp. gr. 1·1383 at 14°. When treated with hydrocarbons it forms compounds of the type $CHX_2\cdot CCl_2$ (Fritsch, Annalen, 279, 219; Wiechell, Annalen, 279, 337; Buttenberg, Annalen, 279, 324).

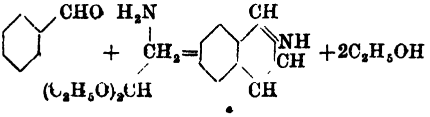
Trichloracetal $CCl_3\cdot CH(OC_2H_5)_2$ (Byasson, Bull. Soc. chim. 32, 304; Wurtz, Frapolli, J. 1872, 438); b.p. 197°; 204·8° at 758·7 mm. Paternò, Pisati J. 1872, 303), sp. gr. 1·2813. When heated with concentrated sulphuric acid it yields chloral.

Trichloracetal $C_6H_{11}Cl_3O_2$. Obtained by the action of chlorine on alcohol (Lieben, Paternò, Krey, *l.c.*); crystallises in monoclinic needles resembling caffeine; m.p. 89°.

Monobromacetal (Pinner, Ber. 5, 149; Wislicenus, Annalen, 192, 112; Fischer a. Landsteiner, Ber. 25, 2551; Freundler a. Ledru, Compt. rend. 1905, 140, 794); b.p. 81°–82° at 27–28 mm. (Freundler). According to F. a. L. a cheap method of making monobromacetal is by brominating paraldehyde at 0° with constant shaking, mixing with absolute alcohol, and after standing 12 hours pouring into an ice-cold sol. of potassium carbonate. The separated oil is dried and fractionated *in vacuó*.

Monoiodoacetal, b.p. 100° at 10 mm.; sp. gr. 1·4944 at 15° (Hesse, Ber. 1897, 30, 1438).

Aminoacetal $NH_2\cdot CH_2\cdot CH(OC_2H_5)_2$ was first prepared by Wohl by treating chloracetal with ammonia (Ber. 21, 616). It can also be prepared by reducing nitroacetal (b.p. 14°: m.p. 89°–91°, from iodoacetal and silver nitrite) with sodium and alcohol. It forms a colourless oil of b.p. 172°–174°, with a strong amine smell; it emulsifies with a little water, but dissolves on adding more water, and can be separated from the solution by the addition of solid alkali. It is of some importance as a synthetic agent, as it readily condenses with aromatic aldehydes to form derivatives of isoquinoline:



Substituted alkylaminoacetals are also known (Paal and van Gomber, Archiv. der Pharm. 246, 306; Störmer and Prall, Ber. 30, 1504).

Acetal sulphide (acetalyl sulphide) $[(C_2H_5O)_2\cdot CH\cdot CH_2)]_2S$ has been prepared by Fischer (Ber. 42, 1070) by heating chloracetal with aqueous potassium sulphide at 120°–150° C. It forms a colourless liquid, b.p. 280° C. (750 mm.). It dissolves readily in water, from which it can be precipitated by salt, and is decomposed by boiling with 1 p.c. hydrochloric acid.

Chloro-triethyl-phosphinoacetal is described by Caldwell (Trans. Chem. Soc. 109, 283). Prepared by heating monochloracetal and triethylphosphine; it forms a viscous liquid of overpowering odour. The corresponding bromo compound is also described. They are hydrolysed to the respective aldehydes.

Dipropyl acetal $CH_3\cdot CH(O\cdot C_3H_7)_2$, b.p. 147°; sp. gr. 0·825 (22°) (de Girard, Compt. rend. 91, 629).

Di-n-butyl acetal $CH_3\cdot CH\cdot(OC_4H_9)_2$, b.p. 198°–200° (King and Mason, Eng. Pat. 101428).

Di-iso-butyl acetal $CH_3\cdot CH(OC_4H_9)_2$, b.p. 170°; sp. gr. 0·816 (22°) (Claus and Trainer, Ber. 19, 3006; de Girard, Compt. rend. 91, 629).

Di-iso-amyl acetal $CH_3\cdot CH(OC_5H_{11})_2$, b.p. 211°; sp. gr. 0·835 (15°) (Alsberg, Jahresb. f. Chemie. 1864, 485; Claus and Trainer, *l.c.*).

Various other acetals have been prepared, but are for the most part unimportant; the following may be noted:—

Acrolein diethyl acetal $CH_2 : CH\cdot CH(OC_2H_5)_2$, b.p. 123·5°; sp. gr. 0·8453 (15°); sparingly soluble in water, miscible with alcohol and ether; hydrolysed by cold hydrochloric acid (Wohl, Ber. 31, 1796. For reactions, *see* Wohl, *l.c.*; Wohl and Emmerich, Ber. 33, 2761; Wohl and Schweitzer, Ber. 40, 92). Acrolein itself reacts with orthoformic ester, &c., to yield the *ethoxy derivative of propionaldehyde acetal* $CH_2\cdot(OC_2H_5)\cdot CH_2\cdot CH(OC_2H_5)_2$, b.p. 184°–186° (Claisen, Ber. 29, 2933; 31, 1014; Fischer and Giebe, Ber. 30, 3056). Similarly, crotonaldehyde yields *β-ethoxy-butyraldehyde acetal* $CH_3\cdot CH(OC_2H_5)\cdot CH_2.CH(OC_2H_5)_2$, b.p. 73°–74°/ 14 mm. (Claisen, *l.c.*).

Crotonaldehyde diethyl acetal, see Wohl and Frank (Ber. 35, 1904).

Propargylaldehyde diethyl acetal

$$CH : C\cdot CH(OC_2H_5)_2$$

forms an oil with a camphor-like odour, b.p. 140° (Claisen, Ber. 29, 2933; 31, 1015, 1022; 36, 3664, 3668; 40, 3907).

Glycerine aldehyde acetal

$$CH_2(OH)CH(OH)\cdot CH(OC_2H_5)_2$$

from acrolein acetal (Wohl, Ber. 31, 1799).

Acetals derived from ketones can be obtained by the action of the hydrochlorides of formimino-ethers or phenylacetimino-ethers (Claisen, Ber. 31, 1012; 40, 3908; Reitter and Hess, Ber. 40, 3023).

Acetone dimethyl acetal $(CH_3)_2\cdot C(OCH_3)_2$, b.p. 83.

Acetone diethyl acetal $(CH_3)_2\cdot C(OC_2H_5)_2$, b.p. 114°.

Glycol acetal, see Pinner (Ber. 5, 150), Verley, (Chem. Zentr. 1899, ii. 919).

Ethyl glyoxal acetal $C_2H_5O{\cdot}CH(OC_2H_5)_2$, b.p. 62°–68° / 10–12 mm. (Dakin and Dudley, Trans Chem. Soc. 105, 2453; *cf.* also Am. Chem. Abstr. 7, 3343; 8, 2252).

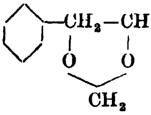
The monosaccharides form derivatives termed glucosides (*q.v.*), which are related to acetals, and it is probable that the true acetals are intermediate products in their formation:

$$HO{\cdot}CH_2{\cdot}[CH(OH)]_x{\cdot}CHO+2HOCH_3$$
$$=H_2O+HO{\cdot}CH_2[CH(OH)]_x{\cdot}CH(OCH_3)_2$$

and these acetals then split off one molecule of alcohol to form the glucosides (E. Fischer, Ber. 28, 1145), which are thus the cyclic-γ-anhydro derivatives of the half-acetals of the monosaccharides.

Aromatic acetals. The mono- and di- acetal derivatives of catechol are obtained by heating the monosodium derivative of catechol with monochloracetal (Moreau, Compt. rend. 126, 1656).

Verley describes the production of methyl acetals of aromatic glycols which are jasmine perfumes, and may be prepared synthetically or from natural extract of jasmine, which consists essentially of the methyl acetal of phenyl glycol (Eng. Pat. 4779, 1898); this substance:

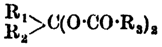


is produced by heating phenyl glycol and formic aldehyde with dilute sulphuric acid. It forms an oil, b.p. 101° / 12 mm., and is identical with the natural perfume. If acetaldehyde be used in place of formaldehyde the ethyl acetal is formed, b.p. 103° / 12 mm.

Diethylbenzaldehyde acetal $C_6H_5{\cdot}CH(OC_2H_5)_2$ may be prepared by the method of Fischer and Giebe (*l.c.*) by treating the aldehyde with 5 times its weight of 1 p.c. ethyl alcoholic hydrochloric acid, and heating to 100° for 60 hours, cooling, diluting with water, and extracting with ether; or, better, by Claisen's method: 37·5 grams benzaldehyde, 57 grams orthoformic ester, and 49 grams alcohol, and 0·75 gram ammonium chloride are refluxed for 10 minutes. The product is then distilled from the accompanying formic ester (b.p. 82°), and after further purification with potassium carbonate is fractionated, the acetal distilling over between 217° and 223°. Yield 62 grams or 97 p.c. of theory. A trace of hydrochloric acid may also be used as a catalyst in place of the ammonium chloride (Claisen, *l.c.*).

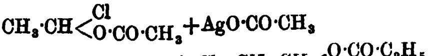
(*b*) *Acidyl derivatives of* gem-*Glycols.*

The diacyl derivatives corresponding to the true acetals:



$$\genfrac{}{}{0pt}{}{R_1}{R_2}{>}C(O{\cdot}CO{\cdot}R_3)_2$$

(R_1 and R_2=alkyl or hydrogen) have hitherto been of slight importance in industry; recently, however, the diacetyl esters of ethylidene glycol have come into prominence as a means for the production of acetic anhydride. They may be prepared by condensing acid chlorides with carbonyl compounds to α-chloralkyl fatty esters, and then treating these with silver or potassium salts of the same or different acids

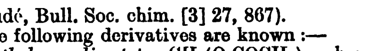


$$CH_3{\cdot}CH{<}\genfrac{}{}{0pt}{}{Cl}{O{\cdot}CO{\cdot}CH_3}+AgO{\cdot}CO{\cdot}CH_3$$
$$=AgCl+CH_3{\cdot}CH{<}\genfrac{}{}{0pt}{}{O{\cdot}CO{\cdot}C_2H_5}{O\,CO{\cdot}CH_3}$$

(Schiff, Ber. 9, 306; Geuther and Rübencamp, Annalen, 225, 273). Acidyl derivatives of methylene glycols can be obtained by treating methylenedihalogenides with the silver salts of fatty acids:

$$CH_2I_2+2AgO{\cdot}COCH_3=2AgI+CH_2(O{\cdot}CO{\cdot}CH_3)_2$$

(Butlerow, Annalen, 107, 111; Arnhold, Annalen, 240, 204), or by condensing polyoxymethylenes with acid chlorides or anhydrides in presence of zinc chloride



$$\genfrac{}{}{0pt}{}{R{\cdot}CO}{R{\cdot}CO}{>}O+CH_2O=\genfrac{}{}{0pt}{}{R{\cdot}CO{\cdot}O}{R{\cdot}CO{\cdot}O}{>}CH_2$$

(Descudé, Bull. Soc. chim. [3] 27, 867).

The following derivatives are known:—

Methylene diacetate $CH_2(O{\cdot}COCH_3)_2$, b.p. 170° (Butlerow, Annalen, 107, 111; Descudé, Bull. Soc. chim. [3] 27, 1215).

Ethylidene diacetate $CH_3{\cdot}CH(OCOCH_3)_2$, b.p. 169°; sp. gr. 1·073 (15°) (Geuther, Annalen, 106, 249; Schiff, Ber. 9, 306; Franchimont, Rec. trav. chim. 1, 248; Geuther and Rubencamp, Annalen, 225, 273).

Ethylidene dipropionate $CH_3CH(OCOC_2H_5)_2$, b.p. 192°; sp. gr. 1·020 (15°) (Geuther and Rubencamp, *l.c.*; *cf.* also Eng. Pat. 14246, 1913).

Ethylidene dibutyrate $CH_3{\cdot}CH(OCOC_3H_7)_2$, b.p. 215°; sp. gr. 0·985 (15°) (Geuther and Rubencamp, *l.c.*).

Ethylidene di-isovalerianate

$$CH_3{\cdot}CH(OCO{\cdot}C_4H_9)_2,$$

b.p. 225°; sp. gr. 0·947 (15°) (Geuther and Rubencamp, *l.c.*).

Of these *ethylidene diacetate* is by far the most important; it is now made technically by passing acetylene into acetic acid containing a mercury salt as catalyst

$$C_2H_2+2CH_3{\cdot}COOH=CH_3{\cdot}CH(O{\cdot}COCH_3)_2$$

The Chemisch Fab. Griesheim Elektron (Eng. Pat. 14246, 1913) claim the production of esters of ethylidene glycol and vinyl alcohol by the action of acetylene upon compounds containing carboxyl groups in the presence of mercury salts; the esters are stated to be solvents for cellulose esters; in an example, 250 grams of anhydrous acetic acid are mixed with 10 grams mercury sulphate and, at 60°–80° C., dry acetylene is passed through until action ceases. The product on distillation yields 80–90 p.c. of the theoretical amount of the ester.

Boiteau (Eng. Pat. 15919, 1914) claims a modification consisting in forming the required catalyst in the substance heated. For example, mercuric oxide, or a mercury salt of a weak acid, such as acetic acid, is dissolved in glacial acetic acid, sulphuric acid is then added, and acetylene passed in.

The Soc. Chim. des Usines du Rhône describe (Eng. Pat. 112765) a further modification in which ethylidene diacetate is prepared by the reaction of acetylene on glacial acetic acid in the presence of mercury acetate and aromatic or aliphatic sulphonic acids. In Eng. Pat. 112766 the same patentees claim also the use of mercury acetate and sulphuric esters, *e.g.* methylene sulphate.

The diacetic ester obtained by any of these processes splits up on heating into acetaldehyde (or paraldehyde) and acetic anhydride:

$$CH_3{\cdot}CH(O{\cdot}CO{\cdot}CH_3)_2 = CH_3CHO + O(CO{\cdot}CH_3)_2$$

Thus, the Bosnische Elektrizitäts A. G. (Eng. Pat. 23190, 1914) claim the production of acetic anhydride by heating ethylidene diacetate above its boiling-point, or by heating it with catalysts, such as sulphuric acid or mercuric sulphate. The Soc. Chim. des Usines du Rhône (Eng. Pat. 10906) describe the production of acetic anhydride and paraldehyde by heating ethylidene diacetate under reduced pressure in the presence of catalysts, such as acids or acid salts. For instance, 400 parts of the ester and 8 parts of sulphuric acid (66° Bé.) are placed in a suitable vessel and heated to 70°–80° C. at a pressure of 100 mm. In two hours 350 parts of a mixture of paraldehyde and acetic anhydride distil over. (The boiling-point of ethylidene diacetate at 100 mm. is about 115° C.) (Cf. also Eng. Pat. 131399, Soc. Chim. des Usines du Rhône.) The diacetate can also be made by heating acetaldehyde with acetic anhydride (Geuther, Annalen, 106, 249), but the yield is poor, and the method is without technical importance.

Benzylidene diacetate $C_6H_5CH(OCOCH_3)_2$, m.p. 45°–46°; b.p. 220° (225°–230°), can be prepared by heating 20 grams benzyl chloride with 35 grams lead peroxide and 80 c.c. boiling acetic acid (Bodroux, Bull. Soc. chim. [3] 21, 331); by refluxing 20 grams benzaldehyde with 20 grams acetic anhydride and 10 grams acetic acid for 3 hours at 150°–180° (Nef, Annalen, 298, 277), or by passing air through a mixture of benzaldehyde and acetic anhydride containing a trace of acetic acid (Freer and Novy, Am. Chem. J. 27, 160). In complete absence of acetic acid no action occurs. It is only slowly attacked by boiling with sodium carbonate solution or by treatment with soda lye, but is hydrolysed by cold concentrated sulphuric or nitric acids. (*Cf.* also Wicke, Annalen, 102, 368; Geuther, *ibid.* 106, 251; Limpricht, *ibid.* 139, 321; Beilstein and Kuhlberg, *ibid.* 146, 323; and Zeit. f. Chemie. 1867, 277; 1868, 172; Chem. Zentr. 1908, 1, 1831; 1909, 2, 1220.)

F. A. M.

ACETAMIDE C_2H_5NO, or $CH_3.CONH_2$.

(Hofmann, Ber. 15, 980; Schulze, J. pr. Chem. [2] 27, 512; Keller, J. pr. Chem. [2] 31, 364; Aschan, Ber. 31, 2344; Kündig, Annalen, 105, 277; Abel, J. Soc. Chem. Ind. 1899, 515.)

Acetamide is usually prepared by the dry distillation of ammonium acetate; a better yield (91·7 p.c.) and a purer product is obtained by distilling ammonium diacetate in the special apparatus described by François (J. Pharm. Chim. 23, 230). Between 135° and 195° acetic acid and water are evolved, and at 195°–222° some acetamide passes over. When the temperature remains constant at 222° the distillation is stopped, the residue being pure acetamide. A nearly theoretical yield is obtained by saturating a mixture of ethyl acetate and ammonia with dry ammonia gas at −10°, and after standing, fractionating *in vacuô* (Phelps, Amer. J. Sci. 24, 429).

Acetamide forms white hexagonal crystals which are odourless when pure, and melt at 81°–82° (Hofmann, Ber. 14, 2729; Mason, Chem. Soc. Trans. 1889, 107; Meyer, Ber. 22, 24; Forster, Chem. Soc. Trans. 1898, 791; Nicol, Zeitsch. anorg. Chem. 15, 397), boils at 222° (cor.) [Kündig], is readily soluble in water, and when heated with acids or alkalis is converted into acetic acid and ammonia (Coninck, Compt. rend. 121, 893; 126, 907; 127, 1028; Dunstan a. Dymond, Chem. Soc. Trans. 1894, 220; Guebet, Compt. rend. 129, 61). Chlorine, led into fused acetamide, yields acetchloramide $CH_3{\cdot}CONHCl$; and bromine, in the presence of dilute aqueous potash or soda yields acetbromamide, which on distillation with concentrated aqueous soda is converted into methylamine (Hofmann, Ber. 15, 408); Buchner and Papendieck, Ber. 25, 1160; Selivanoff, Ber. 26, 423; François, Compt. rend. 147, 680; 148, 173; Behrend a. Schreiber, Annalen, 318, 371). Acetamide acts both as a base and an acid (Pinner and Klien, Ber. 10, 1896), combining with hydrogen chloride or nitric acid, and forming compounds in which a metal takes the place of one atom of hydrogen, as $C_2H_3O{\cdot}NHAg$ (Strecker, Annalen, 103, 321; Tafel and Enock, Ber. 23, 1550; Blacher, Ber. 28, 432; Hofmann and Bagge, Ber. 41, 312; Titherley, Chem. Soc. Trans. 1897, 467). According to Forster (Chem. Soc. Trans. 1898, 783), mercury acetamide is a powerful dehydrogenising agent and owing to its tendency to exchange its mercury for hydrogen when the latter is attached to nitrogen, particularly when hydroxyl groups are in proximity, it can be employed as a convenient means of detecting primary and secondary hydrazines and primary hydroxylamines. It has also a marked tendency to form additive compounds (Morgan, Chem. Soc. Proc. 1906, 23). The hydrogen in the NH_2 group has also been replaced by alkyl groups (Titherley, Chem. Soc. Trans. 1901, 396, 411, 413). Acetamide forms molecular compounds of the type $CH_3{\cdot}CONH_2,X$, where X = an organic or inorganic acid or an inorganic salt (Titherley, *l.c.*; Topin, Ann. Chim. Phys. [7] 5, 99). When acetamide is treated with formaldehyde, paraldehyde, or trioxymethylene, condensation products of the type $R{\cdot}NH{\cdot}CH_2OH$ are obtained; these products are of value as antiseptics and as solvents for uric acid (J. Soc. Chem. Ind. 1906, 283). Mono-, di-, and trichloracetamide (Willm, Annalen, 102, 110; Geuther, J. 1864, 317; Pinner and Fuchs, Ber. 10, 1066; Malaguti, Annalen, 56, 286; Cloëz, Annalen, 60, 261; Bauer, Annalen, 229, 165; Dootson, Chem. Soc. Trans. 1899, 171; Swartz, Chem. Zentr. 1899, [i.] 588; Clermont, Compt. rend. 133, 737). Bromo-dialkyl-acetamide (J. Soc. Chem. Ind. 1904, 1238) and other halogen derivatives have also been prepared (Selivanoff, J. Russ. Phys. Chem. Soc. 24, 132; Broche, J. pr. Chem. [2], 50, 97; Conrad, Ber. 29, 1042; Zincke and Kegel, Ber. 23, 230. Willstätter, Ber. 37, 1775; Steinkopf, Ber. 41, 3571; Swartz, *l.c.*; Francesconi, Gazz. chim. ital. 33, 226; Ratz, Monatsh. 1904, 25, 687; Einhorn, Annalen, 343, 203; Finger, J. pr. Chem. 1906, [ii.] 74, 153).

The acetamido β-naphthaquinones and some of their halogen derivatives which may be used in dyeing (Kehrmann and Zimmerli, Matis, and Locker, Ber. 31, 2405; Kehrmann and Aebi, Ber.

32, 932; Kehrmann and Wolff, Ber. 33, 1538) and other acetamide derivatives have been prepared (J. Soc. Chem. Ind. 1894, 60; Lumière, Bull. Soc. chim. 1903, iii. 30, 966; Ratz, Monatsh. 26, 1487; Miolati, Gazz. chim. ital. 23, 190).

Diacetamide $C_4H_7NO_2$, or $NH(C_2H_3O)_2$ and its derivatives (*see* Gautier, Z. 1869, 127; Hofmann, Ber. 14, 2731; Hentschel, Ber. 23, 2394; Curtius, Ber. 23, 3037; Mathews, Amer. Chem. J. 20, 648; König, J. pr. Chem. 1904, [ii.] 69, 1; Troeger, J. pr. Chem. 69, 347; *Triacetamide* $C_6H_9NO_3$, or $N(C_2H_3O)_3$ and its derivatives (*see* Wichelhaus, Ber. 3, 847).

ACETANILIDE $C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3$, also known as *Antifebrin*, is prepared by heating together glacial acetic acid and aniline for some time.

For an account of its preparation on a manufacturing scale, *see* Müller, Chem. Zeit. 1912, 36, 1055: quoted by Cain, 'Manufacture of Intermediate Products for Dyes,' Macmillan & Co., p. 51.

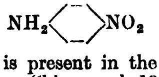
By substituting thioacetic acid for acetic acid the reaction proceeds more rapidly and at a lower temperature (Pawlewski, Ber. 1898, 661). Acetanilide may also be prepared by heating 1 part of aniline with 1¾ parts of dilute acetic acid or of crude pyroligneous acid under pressure at 150°–160° (Matheson & Co., Eng. Pat. 6220 and D. R. P. 98070; J. Soc. Chem. Ind. 1897, 559).

A simple laboratory method consists in gently boiling a mixture of equal weights of aniline and acetic acid with 2 3 p.c. of zinc chloride under a reflux condenser for 3 hours, when the whole is poured into water and the acetanilide re-crystallised from water. The use of pure aniline obviates the necessity of decolorising with animal charcoal.

The substance melts at 114·2° (Reissert, Ber. 1890, 2243), at 115°–116° (Hantzsch and Fresse, Ber. 1894, 2529), and boils without decomposition at 303·8° (corr.) (Pictet and Crépieux, Ber. 1888, 1111), at 305° (corr.) (Perkin, Chem. Soc. Trans. 1896, 1216); it is soluble in hot water, alcohol, or ether.

Acetanilide is hydrolysed at 100° by caustic potash or by hydrochloric acid, but not by sulphuric acid (Hantzsch and Fresse, Ber. 1894, 2529); it is rapidly decomposed by chromic acid, liberating carbon dioxide, and producing colouring matters (De Coninck, Compt. rend. 1899, 503). It reacts with zinc chloride at 180° with the formation of the yellow dye *flavaniline* (Braütigam, Pharm. Zeit. 44, 75).

By treating a solution of acetanilide in sulphuric acid with a mixture of nitric and sulphuric acids and hydrolysing the product, it is converted into *p*-nitroaniline



Acetanilide is present in the urine of cows (Petermann, Ann. Chim. anal. 1901, 165). It is largely used in headache powders and to adulterate drugs, such as phenacetin. It seems to act physiologically by the slow liberation of aniline, and may thus give rise to aniline poisoning. It is oxidised to some extent in the body to *p*-aminophenol. For methods of estimation *v.* Puckner, Ph. Rev. 1905, 302, and Seidell, Amer. Chem. J. 1907, 1091. The following reactions may be used for detecting its presence: (1) bromine water added to a solution of acetanilide in acetic acid gives a white crystalline precipitate of *p*-bromacetanilide, m.p. 167°; (2) evaporation of a solution to dryness with mercurous nitrate gives a green mass, changing to blood red on addition of a drop of concentrated sulphuric acid; (3) ferric chloride gives no blood-red colouration with acetanilide, thus distinguishing it from phenacetin and antipyrine.

Derivatives.—Chloracetanilides (Jones and Orton, Chem. Soc. Trans. 1909, 1056); Nitroacetanilides (Holleman and Sluiter, Rec. trav. chim. 1906, 208).

ACETIC ACID. *Acide Acétique. Essigsaure. Acidum Aceticum.* $C_2H_4O_2$ *i.e.* $CH_3{\cdot}COOH$, or $C_2H_3O{\cdot}OH$.

Acetic acid occurs in nature in the juices of many plants, especially trees, either as free acid or, generally, as the calcium or potassium salt; and, in the form of organic acetates, in the oils from many seeds. It is stated to be present in larger quantities when the plants are kept from the light. It exists in certain animal fluids; Béchamp states it to be a normal constituent of milk. Gmelin and Geiger have found it in mineral waters, doubtless from the decomposition of organic matter.

Being a very stable body both at the ordinary and at high temperatures, it is found as a product of the decomposition or destructive distillation of many organic substances. Acetic acid was first shown by Lavoisier to be formed by the oxidation of alcohol. Its true composition was ascertained by Berzelius in 1814, and in 1821 E. Davy (Schweigger's J., 1821, 1, 340) proved that it was formed, together with water, by the oxidation of alcohol, without the formation of carbonic acid as had been previously supposed. It was this observation which led Dobereiner (*ibid.* 8, 321) to explain acetic fermentation as a simple process of oxidation.

Preparation.—Acetic acid is produced by the oxidation, decomposition, and destructive distillation of many organic bodies. The greater part of that used in commerce is obtained by the destructive distillation of wood.

Hawley and Palmer (Eighth Int. Cong. Appl. Chem. 1912 [4] Orig. Comm. 6, 138) have shown that the temperature within the retort above 320° has but little influence on the yield of acetic acid obtained in the destructive distillation of wood. They obtained the following average amounts of 100 p.c. acid from samples of the body wood and slabs (*i.e.* body wood and bark together) of the hard woods commonly used for the distillation in U.S.A.: Birch, 6·50; beech, 5·55; maple, 4·95; red gum, 5·16; chestnut, 5·32; hickory, 4·61; and oak, 4·70 p.c., calculated on the dry weight of the wood.

Acetic acid may also be obtained by boiling sawdust with water under a pressure of 6 atmos. Under these conditions Bergström (Papierfabr. 1913, 11, 305) obtained from 1·17 to 1·37 p.c. of acetic acid, and 0·19 to 0·23 p.c. of formic acid from coniferous woods (spruce, pine), and more than twice as much acetic acid, and rather less formic acid from birch and other deciduous woods. Analogous results were obtained by destructive distillation of the woods, and, for this reason lime acetates made from the wood of deciduous trees contain less formic acid than those prepared from coniferous wood.

In Raisin's process (Fr. Pats. 446871 and 446878, 1911) sawdust is hydrolysed at about 150° by means of sulphurous acid and steam, and the acid vapours are condensed and neutralised with soda. Calvert (Eng. Pat. 10687, 1913) claims a method of producing acetic acid by the destructive distillation of coffee husks in a retort provided with a screw conveyor.

In 1910 the amount of acetate of lime produced in U.S.A. from hard woods was 152,779,000 lbs., and the amount of acetic acid in 1909 was 51,963,000 lbs., the bulk of which was used in the manufacture of dyes and paper (Palmer, Oil, Paint, and Drug Rep. March 9, 1914).

A method of obtaining acetic acid by the destructive distillation of coal, lignite, &c., has been patented (Behrens, Ger. Pat. 275049, 1913). Ethylenic compounds are isolated from the gases by means of sulphuric acid, mixed with carbon dioxide, and heated to about 400°. About 75 p.c. of the ethylenic compounds are thus converted into acetaldehyde, which is then oxidised to acetic acid (*vide infra*).

Manufacture of Acetic Acid from Alcohol.—Alcohol may be converted into acetic acid by powerful oxidising agents, such as chromic acid, nitric acid, &c. Advantage may be taken of the fact that spongy platinum or platinum black has the property of absorbing oxygen, and thus acting as a powerful oxidising agent. If spongy platinum be placed over a vessel of alcohol with free access of air, the platinum absorbs at the same time the oxygen and the alcohol vapour, which combine and produce acetic acid and water :—

$$\underset{\text{Alcohol.}}{CH_3CH_2OH}+O_2=\underset{\text{Acetic acid.}}{CH_3COOH}+OH_2$$

In addition to acetic acid, aldehyde (acetic aldehyde) is produced, which is intermediate in composition between alcohol and acetic acid. It is formed by the removal of two atoms of hydrogen from the alcohol and their replacement by an atom of oxygen :—

$$\underset{\text{Alcohol.}}{CH_3{\cdot}CH_2{\cdot}OH}+O=\underset{\text{Aldehyde.}}{CH_3{\cdot}CHO}+H_2O$$

In presence of excess of oxygen aldehyde forms acetic acid. Aldehyde is a very volatile liquid, and is liable to be lost before its conversion into acetic acid ; it is therefore necessary in all cases where acetic acid is produced by the oxidation of alcohol to allow free access of air.

This method produces a very pure acetic acid, but on account of the initial cost of the platinum (which, however, is not in any way injured by use) it is not extensively used on the manufacturing scale.

Numerous patents have been taken out for the oxidation of alcohol or acetaldehyde to acetic acid. In Behrens' process (Ger. Pat. 223308, 1908) alcohol is oxidised to aldehyde by the action of air in the presence of platinum as catalyst. The aldehyde is separated by fractional distillation, and, after the addition of dilute sulphuric acid to make it electrically conductive, it is electrolytically oxidised. The bulk of the acid produced may then be recovered by a single distillation in a column still.

In a later patent of Behrens (Eng. Pat 28839, 1910), the alcohol is oxidised by the catalytic action of zinc oxide at about 350°, and the aldehyde then oxidised by contact with oxygen in an absorbing tower.

According to another process patented by the Chem. Fabr. Griesheim-Elektron (Eng. Pat. 17424, 1911), acetaldehyde is oxidised by means of air in the presence of acetic acid or a chlorine derivative thereof, a catalyst, such as vanadium pentoxide, or uranium oxide, being also used to promote the reaction ; or the aldehyde may first be oxidised by excess of oxygen (Eng. Pat. 8076, 1912).

The addition of small amounts of manganese compounds promotes the oxidation, without the risk of explosion attending the use of compounds of vanadium, chromium, or cerium (Consortium Elektrochem. Ind. ; Fr. Pat. 460971, 1913).

By mixing the acetaldehyde with about 1 p.c. of ceric oxide or other catalyst, and treating it with oxygen under a pressure of about 2 atmospheres, or with air at about 5 atmospheres, about 95 p.c. of the theoretical yield of anhydrous acetic acid is obtainable (Farbenwerke vorm. Meister, Lucius and Bruning ; Eng. Pat. 10377, 1914).

The Badische Anilin u. Soda Fabr. (Ger. Pat. 294724, 1914) has claimed a process of oxidising acetaldehyde by means of air or oxygen in the presence of iron compounds and organic salts of alkalis, alkaline earths, aluminium or magnesium. The reaction is stated to take place rapidly, and without the aid of heat, whilst no per-acids are produced.

In Hibbert's process (U.S. Pat. 1230899, 1917), wood charcoal previously saturated with strong acetic acid is used as the contact material for the oxidation of acetaldehyde by means of oxygen.

Manufacture from Acetylene.—A French patent (360249, 1905) describes the preparation of acetic acid from acetylene. Acetylene is passed into a solution of a normal mercuric salt, which precipitates mercury acetylide. The liquid is then boiled, when aldehyde is formed and the mercuric salt re-formed. The aldehyde is then oxidised to acetic acid.

An electrolytic process of oxidising acetylene to acetic acid has been patented by the Farbenfabr. vorm. Bayer u. Co. (Fr. Pat. 467778, 1913), the acetylene being oxidised by the use of a solution of sulphuric acid or other acid as electrolyte, in presence of a mercury compound. In another patent by the same firm (Fr. Pat. 467515, 1914), the acetylene is passed through a solution of hydrogen peroxide, or a persulphate at about 30°–40°, in the presence of mercury or a mercury compound. The resulting liquid will contain about 25 p.c. of acetic acid.

The oxidation process may also be accelerated by the use of other catalysts in addition to mercury, with or without the simultaneous application of pressure (Fr. Pat. 471253, 1914).

Acetic acid may also be produced without preliminary isolation of acetaldehyde by oxidising acetylene in an organic acid medium, such as acetic acid, by means of oxygen, acting in the presence of the requisite quantity of water and of a catalyst, such as iron oxide or vanadium pentoxide. The best results are obtained by introducing the acetylene and oxygen alternately in small quantities into the acid medium (Chem.

Fabr. Griesheim-Elektron, Fr. Pat. 473158, 1914).

Acetic Acid by Fermentation Processes.—Several species of bacteria are capable of converting alcoholic liquids into acetic acid. The species first recognised, as forming films on sour wine and vinegar, was termed *Mycoderma* by Persoon, in 1822, although he did not associate them with the development of acidity. Even since it has been recognised that the pellicle was not the product of yeasts or mould-fungi the name has survived, and is still frequently used as a generic term for the acetic bacteria. The views of Stack, published in 1863, that the *Mycoderma aceti*, or 'mother-of-vinegar,' consisted of an aggregation of bacteria was not accepted in 1868 by Pasteur: but Cohn, in 1872, included these micro-organisms among the bacteria.

Hansen, in 1878 (*see* Compt. rend. Lab. Carlsberg, 1894 [iii.]; 1900 [v.]), isolated three species, which he termed *Bacterium aceti*, *B. Pasteurianum*, and *B. Kützingianum*, and showed that they differed from one another in form and in the nature of the pellicles which they produced when grown in alcoholic culture media.

Numerous other species of acetic bacteria have been described, such as *Bacillus xylinus* (Brown, J. Chem. Soc. 1886, 30, 432; Proc. Chem. Soc. 1887, 87); *B. oxydans*, *B. acetosus*, *B. acetigenus*, *B. curvus*, *B. xylinoides*, &c. (Henneberg, Centralbl. f. Bakt. 1909, 24, 13); and *B. rancens* (Beijerinck; Centralbl. f. Bakt. 1898, 4, 209). Although each of these differed in properties and in producing different involution forms, there is some reason for concluding that some, at least, of them are not distinct species, but varieties modified by their environment.

In 1906 Buchner and Gaunt (Annalen, 1906, 349, 140) separated an acetic enzyme by extracting the zoogloeal pellicle of 'mother-of-vinegar' with acetone. The preparations were capable of oxidising alcohol to acetic acid, and had also the power possessed by the living bacteria of oxidising propyl alcohol to propionic acid. An enzyme separated in this way from Hansen's *B. aceti* has been shown by Wieland (Ber. 1913, 46, 3327) to be capable of replacing palladium as a catalyst for the oxidation of alcohol into acetic acid.

For the production of acetic acid from alcoholic 'washes' by the action of living acetic bacteria, the liquid must contain a suitable proportion of nutrient substances (phosphates, nitrogenous substances), &c., and there must be a regulated supply of air (*see Manufacture of Vinegar, infra*).

For the manufacture of the so-called 'spirit acid,' a crude vinegar containing from 10 to 12 p.c. of acetic acid is first made by a fermentation process from an artificially prepared wash composed of potato spirit with nutrient substances. This is known as *Essigsprit* or *Spritessig*, and is a common commercial product. It is concentrated by neutralisation with lime, evaporation of the liquid to dryness, and distillation of the crude calcium acetate, as described below. Owing to its more pleasant aroma spirit acid of 80 p.c. strength fetches a higher price in the market than ordinary acetic acid.

A process of obtaining acetic acid by a fermentation process from the Japanese seaweed *Fucus evanescence*, has been described by Takahashi (J. Chem. Ind., Tokyo, 1916, 19, 30). The seaweed is mixed with water and 3 to 5 p.c. of lime, which is added in successive small quantities, and the mixture is kept at 30° for 2 weeks. The yield of acetic acid is increased by the addition of fucose.

Distillation of Acetic Acid.—The *concentrated* or *glacial* acid is usually prepared by the distillation of a dry acetate with an equivalent quantity of strong sulphuric acid, or acid potassium or sodium sulphate.

Sodium acetate is generally used. The anhydrous salt is fused on sheet-iron pans, 6 feet by 4 feet, care being taken that no sparks reach the dried salt, as it would then ignite and burn like tinder. The mass is cooled, broken into small lumps, and distilled with concentrated sulphuric acid. The first portion distilling contains the water, the later portion is collected and cooled; when crystals have formed the still liquid portion is removed, the crystals are melted and redistilled as before, producing the glacial acid.

When a solution of calcium chloride is mixed with a solution of calcium acetate, crystals of calcium aceto-chloride $CaC_2H_4O_2Cl5H_2O$ gradually separate. These crystals may be produced in comparative purity even when impure *brown* acetate of lime is used. To obtain acetic acid ordinary commercial or 'distilled' acetate of lime is mixed with the proper proportion of calcium chloride, and the solution is concentrated by evaporation until it crystallises; the mother liquor is poured from the crystals and concentrated with the production of a second crop of crystals; this is repeated until about four crops have been produced. The crystals are dissolved in water, filtered through animal charcoal, mixed with about 10 p.c. of calcium chloride, and recrystallised. The crystals are distilled with a mixture of 1 part sulphuric acid of sp. gr. 1·84 and 2 parts water, and the acetic acid concentrated in the usual way. The glacial acid may also be prepared by the distillation of di- or acid-acetate of potassium, which, when heated, decomposes into acetic acid and the normal potassium acetate. If ordinary acetic acid be heated with normal potassium acetate, the acid acetate is formed, and a weaker acid at first distils over; as the temperature rises, the diacetate begins to decompose, and the distillate increases in strength until the glacial acid passes over. When the temperature reaches 300° the distillate becomes coloured from the decomposition of the acid (Melsens, Annalen, 52, 274; Compt. rend. 19, 611).

In Chute's method of preparing acetate of lime the vapours from crude pyroligneous acid are brought into contact with a stream of water mixed with lime. The temperature of the liquid is kept at about 100° by the addition of quicklime (U.S. Pat. 939980, 1909).

Scott and Henderson (Eng. Pat. 6711, 1896) purify the crude acetates by boiling with sodium hypochlorite until nearly decolorised. The solution is then cooled and allowed to settle. The clear liquid is decanted and crystallised. The crystals are of great purity.

Another method of removing organic impurities is to boil the crude acetates with lime, an iron salt, and a bleaching agent (Zinkeisen, U.S. Pat. 1213724, 1917).

Scott (Eng. Pat. 12952, 1897) has patented a process which dispenses with lime in the manufacture of acetic acid. He distils the crude acid at 100°, and fractionally condenses the vapours. The acid collects mainly in the first portions.

Crude acetates may be decomposed with H_2SO_4 or HCl, and the acetic acid distilled *in vacuo* (Thompson, J. Soc. Chem. Ind. 1896, 357); or crude acetic acid may be treated with oxygen under pressure, filtered through charcoal and distilled over pure sodium acetate (Schmidt, Eng. Pat. 1896, 25190).

Hochstetter (J. Soc. Chem. Ind. 1902, 1469) prepares pure acetic acid by heating pure sodium acetate with dry HCl at 120°; whilst Plater and Syberg patented a process of obtaining acetic acid by the electrolysis of alkali acetates.

According to the patent process of Farbenfabr. vorm. Bayer u. Co. (Ger. Pat. 220705, 1907) the crude acetate is heated to about 130°, the pressure within the still reduced to about ½ atmosphere, and sulphuric acid introduced. The distillate is claimed to contain only traces of sulphur dioxide.

In Prager's continuous process (Fr. Pat. 449035, 1911) sulphuric acid is sprinkled progressively on the acetate in a series of compartments, the material being mechanically transferred from one compartment to the next, whilst the liberated acetic acid is condensed in the upper part of the apparatus.

Another method of distillation makes use of a hot rotating surface upon which a mixture of acetate and sulphuric acid is mechanically spread. The acetic acid is condensed, and the solid residue is removed from the hot cylinders by means of scrapers (Brauer, U.S. Pat. 1196329, 1916).

Aromatic or radical vinegar.—Before the discovery of pyroligneous acid strong acetic acid was prepared by the distillation of ordinary vinegar, or of crystallised verdigris, whence it was popularly known as *distilled verdigris.* This product, which was distilled from earthenware retorts, formed the *aromatic* or *radical vinegar* of the apothecaries, but the method is now obsolete. It owed its name to its pleasant odour, largely due to acetone, which is always produced when acetates of heavy metals are distilled, but camphor and essential oils were frequently added to increase or modify the smell. Commercial *aromatic vinegar* is now made by adding essential oils and spices to pure diluted acetic acid.

Concentration and Purification.—The acetic acid obtained by the distillation of crude acetates of lime is usually concentrated by the redistillation of united similar fractions in a column still, whilst organic impurities are oxidised by the addition of potassium permanganate or dichromate prior to the distillation.

According to a patent process of the Chem. Fabr. Griesheim-Elektron (Ger. Pat. 230171, 1909) anhydrous copper sulphate is used to dehydrate the acid during the distillation; whilst meta-phosphoric acid is used for the same purpose in another patent (Ger. Pat. 282263, 1914). Galitzenstein (A. angew. Chem. 1916, 29, 148) has described a patent process of obtaining glacial acetic acid from dilute acid by extraction with an immiscible solvent, such as dichloroethylene, and claims that 90 p.c. of the theoretical yield may thus be obtained.

In another process (Harburger Chem. Werke Schon u. Co., Ger. Pat. 292959, 1915) the dilute acid is treated with potassium acetate, and the resulting double compound of potassium acetate and acetic acid which separates from the solution is redistilled.

An electrolytic method of purification (French, U.S. Pat. 1104978, 1914) is based on the decomposition of impurities by means of an electric current, the strength of which is regulated to prevent material decomposition of acetic acid.

Formic acid and tarry matters may be removed by redistilling the crude acid with an equal weight of 70 p.c. sulphuric acid at about 130°, at which temperature formic acid is destroyed, whilst acetic acid is not appreciably attacked (A. Gorhan, U.S. Pat. 1210792, 1917).

Properties.—The strongest acid solidifies at 16·6° (Bousfield and Lowry, Chem. Soc. Proc. 1911, 27, 187) in tabular or prismatic glistening crystals. The glacial acid may be cooled to −10° without solidification, even when agitated, but on the addition of a crystal of the acid the whole solidifies and the temperature rises to 16·7°.

The specific gravity of the crystals at 15°/4° is 1·0607 (Mendeléeff, J. 1860, 7). They melt to a mobile colourless liquid of sp. gr. 1·0543 at 16°/4° (Petterson, J. pr. Chem. [2] 24, 301), 1·0495 at 20°/4° (Brühl), 1·05148 at 18°/4°, and 1·04922 at 20°/4° (Bousfield and Lowry, *l.c.*), which boils at 118·5° at 760 mm. (Perkin), 118·1° (corr.) (Thorpe and Rodger). The liquid is uninflammable, but the vapour burns with a blue flame producing water and carbon dioxide.

Boiling-point of Glacial Acetic Acid under various Pressures (*Landolt*).

Pressure	Boiling point.	Pressure.	Boiling point	Pressure.	Boiling point.
mm.	°C.	mm.	°C.	mm.	°C.
1160	132	560	109	60	48
960	126	360	96	30	31
700	119	160	73		

When passed through a red-hot tube only a small portion is decomposed, producing carbon, acetone, benzene, &c. The strong acid blackens when heated with concentrated sulphuric acid, evolving sulphurous and carbonic anhydrides.

Nitric and chromic acids have no action; for this reason acetic acid is frequently used as a solvent for organic substances such as hydrocarbons, which are to be subjected to the action of chromic acid. Chlorine under the influence of sunlight replaces a portion of the hydrogen, and produces *mono-*, *di-* and *trichloracetic acids.* Similarly, bromine produces *dibromacetic acid.*

Commercial acetic acid contains impurities which react with bromine and chlorine in the dark, whereas pure acetic acid is not attacked by these halogens in the dark. These impurities can be removed by distilling the acid over phosphoric oxide, only traces of acetic anhydride being formed in the process (Orton, Edward, and King, Chem. Soc. Proc. 1911, 27, 120).

Pure acetic acid is not decomposed by direct sunlight, which, however, effects the decomposition of acetaldehyde, with the liberation of methane and carbon monoxide. Direct rays from a mercury vapour lamp decompose both acetaldehyde and acetic acid, the latter yielding carbon monoxide and dioxide and 39 p.c. of combustible gases (Berthelot and Gaudechon, Compt. rend. 1913, 156, 68).

On the addition of water to the glacial acid heat is evolved and the density increases until 20 p.c. of water is present; from this strength to 23 p.c. of water the density remains stationary. Further dilution lowers the density, so that either dilution or concentration from this point will produce an acid of diminished density. An acid containing only 43 p.c. of acid has the same density as the glacial acid. This, together with the slight difference between the density of acetic acid and water, renders it impossible to determine, with any precision, the percentage of acid by means of the hydrometer.

No definite hydrates of acetic acid are known (De Coppet, Ann. Chim. Phys. [7] 16, 275; Colles, Chem. Soc. Trans. 1906, 1247), although the break which occurs in the curve of the solidification points at about 37 p.c. of water suggests the formation of a hydrate

$$C_2H_4O_2+2H_2O$$

The following table shows the density of aqueous acetic acid at 15° and 20° (Oudemans, Jahresber. Fortsch. Chem. 1886, 302):—

DENSITY OF AQUEOUS ACETIC ACID (OUDEMANS).

p.c.	Density		p.c.	Density		p.c.	Density	
	15°	20°		15°	20°		15°	20°
0	0·9992	0·9983	34	1·0459	1·0426	68	1·0725	1·0679
1	1·0007	0·9997	35	1·0470	1·0437	69	1·0729	1·0683
2	1·0022	1·0012	36	1·0481	1·0448	70	1·0733	1·0686
3	1·0037	1·0026	37	1·0492	1·0458	71	1·0737	1·0689
4	1·0052	1·0041	38	1·0502	1·0468	72	1·0740	1·0691
5	1·0067	1·0055	39	1·0513	1·0478	73	1·0742	1·0693
6	1·0083	1·0069	40	1·0523	1·0488	74	1·0744	1·0695
7	1·0098	1·0084	41	1·0533	1·0498	75	1·0746	1·0697
8	1·0113	1·0098	42	1·0543	1·0507	76	1·0747	1·0699
9	1·0127	1·0112	43	1·0552	1·0516	77	1·0748	1·0700
10	1·0142	1·0126	44	1·0562	1·0525	78	1·0748	1·0700
11	1·0157	1·0140	45	1·0571	1·0534	79	1·0748	1·0700
12	1·0171	1·0154	46	1·0580	1·0543	80	1·0748	1·0699
13	1·0185	1·0168	47	1·0589	1·0551	81	1·0747	1·0698
14	1·0200	1·0181	48	1·0598	1·0559	82	1·0746	1·0696
15	1·0214	1·0195	49	1·0607	1·0567	83	1·0744	1·0694
16	1·0228	1·0208	50	1·0615	1·0575	84	1·0742	1·0691
17	1·0242	1·0222	51	1·0623	1·0583	85	1·0739	1·0688
18	1·0256	1·0235	52	1·0631	1·0590	86	1·0736	1·0684
19	1·0270	1·0248	53	1·0638	1·0597	87	1·0731	1·0679
20	1·0284	1·0261	54	1·0646	1·0604	88	1·0726	1·0674
21	1·0298	1·0274	55	1·0653	1·0611	89	1·0720	1·0668
22	1·0311	1·0287	56	1·0660	1·0618	90	1·0713	1·0660
23	1·0324	1·0299	57	1·0666	1·0624	91	1·0705	1·0652
24	1·0337	1·0312	58	1·0673	1·0630	92	1·0696	1·0643
25	1·0350	1·0324	59	1·0679	1·0636	93	1·0686	1·0632
26	1·0363	1·0336	60	1·0685	1·0642	94	1·0674	1·0620
27	1·0375	1·0348	61	1·0691	1·0648	95	1·0660	1·0606
28	1·0388	1·0360	62	1·0697	1·0653	96	1·0644	1·0589
29	1·0400	1·0372	63	1·0702	1·0658	97	1·0625	1·0570
30	1·0412	1·0383	64	1·0707	1·0663	98	1·0604	1·0549
31	1·0424	1·0394	65	1·0712	1·0667	99	1·0580	1·0525
32	1·0436	1·0405	66	1·0717	1·0671	100	1·0553	1·0497
33	1·0447	1·0416	67	1·0721	1·0675			

The addition of a small quantity of water lowers the melting-point of the glacial acid considerably, as shown by the table at top of p 16: Dahms (Ann. Chim. Phys. [7] 18, 141).

The tables on p. 16 of the solidification points of mixtures of acetic acid and water are of use in determining the strength of acetic acid.

Acetic acid is monobasic, but forms both acid and basic, as well as normal salts. It dissolves certain metallic oxides, as those of lead and copper, forming basic acetates.

The action of acetic acid on aluminium is a matter of technical importance, since aluminium stills are in use for distilling the acid. Alumi-

Solidifying-point	Water to 100 parts real acetic acid	Solidifying-point	Water to 100 parts real acetic acid
°C.		°C.	
16·675	0	−3·94	16·38
16·50	0·05	−8·80	21·53
16·06	0·29	−12·80	24·56
14·54	1·15	−18·10	29·97
11·81	2·94	−17·90	30·87
7·21	6·53	−23·87	36·57
2·95	10·33	−24·90	37·52
2·46	10·74	−25·20	39·30
−2·90	15·80	−26·75	40

RÜDORFF'S TABLE OF SOLIDIFICATION POINTS OF MIXTURES OF ACETIC ACID AND WATER (Ber. 1870, 3, 370.)

100 parts of acetic acid mixed with water.	100 parts contain by weight	Solidification point.
		°C.
0·0	0·0	+16·7
0·5	0·497	15·65
1·0	0·990	14·8
1·5	1·477	14·0
2·0	1·961	13·25
3·0	2·912	11·95
4·0	3·846	10·5
5·0	4·761	9·4
6·0	5·660	8·2
7·0	6·542	7·1
8·0	7·407	6·25
9·0	8·257	5·3
10·0	9·090	4·3
11·0	9·910	3·6
12·0	10·774	2·7
15·0	13·043	−0·2
18·0	15·324	2·6
21·0	17·355	5·1
24·0	19·354	7·4

GRIMAUX'S TABLE OF SOLIDIFICATION POINTS OF MIXTURES OF ACETIC ACID AND WATER (Compt. rend. 1873, 76, 486.)

Water.	Acetic acid.	Solidification point.
Per cent.	Per cent.	°C.
7·31	92·69	+ 5·3
13·25	86·75	− 1·4
23·52	76·48	−11·6
31·18	68·82	−19·3
33·56	66·44	−20·5
38·14	61·86	−24·0
44·50	55·50	−22·3
49·38	50·62	−19·8
56·54	43·46	−16·4
61·68	38·2	−14·8
69·23	30·77	−10·9
76·23	23·77	− 8·2
79·22	20·78	− 7·3
81·89	18·11	− 6·4
83·79	16·21	− 5·5

nium is dissolved by boiling 90 p.c. acetic acid with the formation of an insoluble gelatinous basic acetate $Al(O{\cdot}COCH_3)_2OH$, which probably acts as a protective coating upon the surface of aluminium plant. With the dilution of the acid the rate of the solution rapidly increases, and 90 p.c. acetic acid dissolves about 10 times as much aluminium in a given time as 99 p.c. acid, whilst dilute acid attacks the metal very rapidly. Slight variations in the strength often have a pronounced influence on the solvent action, the addition of 0·05 p.c. of water to a corrosive acid being sufficient in some cases to arrest the action (Seligman and Williams, J. Soc. Chem. Ind. 1916, 35, 88).

The most suitable metals for the construction of acetic acid plant are block tin and gun-metal containing a sufficient proportion of tin.

Acetic acid has a pungent sour taste, and when strong blisters the skin. The glacial acid has no action on litmus, but on addition of water becomes powerfully acid. It is not affected by the electric current, probably because a bad conductor, but when a little sulphuric acid is added the current decomposes it, producing, according to Renard (Ann. Chim. Phys. [5] 16, 289), carbon dioxide, carbon monoxide and oxygen. Alkali acetates when electrolysed are decomposed into hydrogen and alkali hydroxide which appear at the negative pole, and ethane and carbon dioxide at the positive pole.

Acetic acid mixes with alcohol and ether in all proportions. It dissolves resins, gelatin, fibrin, albumin, essential oils, &c. Phosphorus and sulphur are somewhat soluble in the warm acid.

Acetic acid is largely used in the preparation of the acetates of copper, aluminium, iron, lead, &c.; as pyroligneous acid in calico printing, and the curing of herrings, hams, &c.; in the preparation of varnishes and colouring matters; in the laboratory and certain industries as a solvent; for domestic use; in photography; and in medicine as a local irritant and to allay fever, and in the form of smelling salts.

Analysis.—Commercial glacial acid should contain not less than 98·9 p.c. of absolute acid. When crystallised it should not re-melt below 14·7°. If 9 volumes oil of turpentine be agitated with 1 volume of acid, no turbidity will be produced if the acid contain 97 p.c. or upwards. Acid of 99·5 p.c. produces no turbidity with any proportion of turpentine (Bardy, Chem. News, 40, 78).

A very delicate test for the presence of water is to mix the acid with an equal bulk of carbon disulphide in a dry tube, and warm with the hand for a few minutes; in presence of a trace of water the liquid becomes turbid.

The commercial acid may contain sulphuric acid, sulphates, sulphurous acid, hydrochloric acid, chlorides, nitrates, arsenic (derived from sulphuric acid), and copper, lead, zinc, iron, and tin derived from the vessels used in the manufacture.

The presence of sulphuric acid or sulphates is shown by the production of a white precipitate with barium chloride. To the filtered solution bromine or chlorine water is added, producing, if sulphurous acid be present, a further precipitate of barium sulphate. Hydrochloric acid and chlorides are detected and estimated by means of silver nitrate.

In testing for metals a considerable bulk of the acid should be evaporated; a few drops of hydrochloric acid are added, and a current of hydrogen sulphide passed through the liquid; a black or brown colouration or precipitate indicates lead or copper. Copper may also be detected in the evaporated liquid by the brown precipitate produced on the addition of potassium ferrocyanide, and estimated by electrodeposition. Iron may also be detected by the ferrocyanide test. To test for zinc, the solution, after the passage of hydrogen sulphide, is filtered, nearly neutralised with ammonia, and sodium acetate added, when zinc will be precipitated as white sulphide. For arsenic Reinsch's, Marsh's, or the electrolytic test may be used.

Small quantities of acetic acid may be recognised by neutralising the liquid with potassium hydroxide, adding arsenious oxide, evaporating to dryness, and heating the residue, when the characteristic smell of cacodyl is evolved.

To determine the free acetic acid in a solution it is usual to titrate a weighed quantity with sodium hydroxide solution standardised against acetic acid of known strength or hydrogen potassium tartrate (Stillwell and Gladding).

As indicator litmus may be used, but as it is rendered blue by the normal sodium acetate, it is preferable to use phenol-phthaleïn, to which that substance is neutral; this is also more sensitive, and, where coloured, the liquid may be considerably diluted without impairing the delicacy of the reaction.

To estimate small percentages of water in acetic acid, the solidifying-point may be determined and the percentage found by the tables before given.

Commercial glacial acetic acid usually contains formic acid in proportions of about 0·02 to 0·8 p.c. Methods of separating and estimating formic, acetic, propionic, and butyric acid in admixture are given in Zeit. anal. Chem. 1899, 38, 217. For the estimation of formic acid, Fincke (Apoth. Zeit. 1910, 727) boils the acid under a reflux condenser with sodium acetate and mercuric chloride, and separates and weighs the precipitated caramel. Another method has been based upon the fact that formic acid will expel acetic acid from acetates. The acid is neutralised with sodium hydroxide, evaporated, and the residue dried at 125°, and weighed. It is then evaporated with formic acid two or three times, and the residue again dried at 125°. The difference between the weights corresponds to the amount of acetic acid expelled. The results for formic acid are about 0·02 p.c. too high, and those for the acetic acid too low (Heermann, Chem. Zeit. 1915, 39, 124). According to the B. P. (1914) test the absence of formates is shown by the acid not darkening immediately when treated with ammonia solution and heated with silver nitrate solution.

Chapman (Analyst, 1899, 24, 114) describes a method for the estimation of *iso*valeric acid in acetic acid.

The presence of acetic anhydride may be ascertained by the red precipitate of amorphous selenium obtained on treating the acid with selenious oxide or sodium selenite, pure glacial acetic acid remaining clear in this test (Klein, J. Ind. Eng. Chem. 1910, 2, 389). Another sensitive test is based upon the fact that acetic anhydride reacts with certain aniline derivatives, notably 2 : 4-dichloro-aniline, to form insoluble anilides, which can be separated and indirectly estimated as chloroamine (Edwards and Orton, Chem. Soc. Proc. 1911, 27, 121).

Aceto-acetic acid may be detected by the violet colouration which it gives with sodium nitroprusside and ammonia, followed by insufficient acid to neutralise all the ammonia (Harding and Ruttan, Biochem. J. 1912, 6, 445).

The acetic acid in acetates may be estimated by distilling about 1 gram of the salt nearly to dryness with 10 c.c. of a 40 p.c. solution of phosphoric acid (free from nitric and other volatile acids); water is added and the distillation repeated to remove the last traces of acetic acid; the distillates are mixed and titrated as above with standard alkali. This method of distillation may also be used for highly coloured solutions of acetic acid where direct titration is not practicable; or the method of distillation with formic acid, described above, may be employed.

Most commercial acetic acid contains traces of tarry substances, though the proportion is much less in acids which have been purified by treatment with permanganate. The permissible limit for such empyreumatic substances in glacial acetic acid is prescribed by a B. P. (1914) test, according to which 2 c.c. of the acid should not decolorise within half a minute a mixture of 3 drops of a 1 p.c. solution of potassium permanganate and 10 c.c. of water.

Manufacture of Vinegar.

The term 'vinegar,' as its derivation implies, was originally applied to wine which had become sour, but is now used to describe all products made by the acetic fermentation of alcoholic liquids, the particular kind of vinegar being usually indicated by a prefix, such as 'wine vinegar,' 'malt vinegar,' 'cider vinegar,' or 'spirit vinegar.' The terms 'beer vinegar' and 'alegar,' which are to be found in the Acts of Parliament, are now obsolete.

From whatever material vinegar is derived the essentials of the process are the same. An alcoholic liquid of a suitable strength must be subjected to the oxidising action of acetic bacteria, in the presence of suitable nutrient substances, and of a regulated supply of air.

Wine vinegar. (Fr. *Vinaigre*; Ger. *Weinessig.*) In the wine district of Orleans, which has been celebrated for centuries for the production of wine vinegar of fine aroma and flavour, the original method was to add a little vinegar to sour wine, and to expose the mixture to the air in open casks. This primitive method was still in use as late as 1876, although most vinegar makers in France had long discarded it for the 'Orleans process,' in which the wine is acetified in a series of casks packed with shavings and provided with holes for the admission of air.

Full-bodied wines are selected for the manufacture, and if they contain above 10 p.c. alcohol they are suitably diluted with weaker wines. The wine, before being fermented, is usually left for some time in contact with beech shavings, on which the lees are deposited, rendering the wine brighter. A certain amount of extractive matter is, however, necessary for the development of the bacteria, and if the wine be old and the matter deposited, the fermentation is much retarded. Wine one year old is preferred.

The 'Vinaigrerie' is usually a building of southern aspect; the rooms in which the process is conducted are low-roofed, and, in order to admit air, the walls are provided with openings which can be closed when the temperature is not sufficiently high.

Sets of casks of well-seasoned oak, bound with iron hoops, each holding from 50 to 100 gallons are supported on their sides in rows about 18 inches from the floor, one set being frequently placed above another, in which case hose nearest the roof are found to work most rapidly. Each cask is bored with two holes in he front end, a larger one, the 'eye,' for the addition of wine or the removal of vinegar, and a small one for the admission of air.

When first used the casks are thoroughly scalded with boiling water to remove extractive natter, filled to a third of their capacity with boiling strong vinegar, and allowed to stand for eight days; from that time wine is added in charges of about 10 pints every eight days until he casks are not more than two-thirds full; after a further interval of 14 days a portion, varying from 10 gallons to half the total bulk, s drawn off and the periodical addition of the wine continued. The temperature of the hambers should be about 25°, and is kept up when necessary with a stove. In order to certain if the fermentation is completed at he end of the usual time, the workman plunges white spatula into the liquid; if a reddish roth adheres, more wine is added and the emperature raised; a white froth indicates he completion of the process. More than eight lays are sometimes required to complete the xidation, in which case stronger wine and a igher temperature may be used. The sluggishess may, however, be due to the casks becoming oul, which occurs usually after about six years' working. The deposit of argol, yeast sediment, &c., is thoroughly removed, and the casks leansed and recharged with hot vinegar as in he case of new casks. Good casks will often ast twenty-five years.

When working satisfactorily each cask will roduce about twice its capacity of vinegar nnually.

Before storing, the vinegar is usually passed hrough the 'rapes' where it is 'brightened' nd the acetification completed.

The drawback of the Orleans process is that is excessively slow, but, on the other hand, he slow working promotes the formation of the sters to which French wine vinegar owes its eputation.

In other parts of France and in Holland and n the Rhine the following method is used. he wine is placed in two large upright tuns bout 9 feet high and 4 feet wide, open to the ir. Each tun has a perforated false bottom bout 12 inches above the true bottom; on this placed a quantity of vine cuttings, stalks, c., so as to expose a large surface for the formaon of the fungus. One of the vats is half, and e other completely, filled. The acetification progresses more rapidly in the former; this, after twenty-four hours, is filled from the full cask, in which the action then increases. This alternate transference is continued daily until the acetification is complete. The most favourable temperature is about 24°. The vinegar is run off into casks containing chips of birch wood on which the lees settle, and in about fourteen days being thus clarified is stored in close casks for the market.

This method is described in a letter published by the Royal Society in 1670 (Phil. Trans. Roy. Soc. 1670, v. 2002).

In Claudon's process of acetification the wine is fermented in a series of superposed closed shallow vessels, so constructed that air currents can be conducted over the surface of thin layers of the wine. This is more rapid than the ordinary Orleans process.

Malt vinegar (*Malzgetreide Bieressig*). The vinegar industry in this country has developed out of the brewing industry, and the connection between the two industries is clearly shown in the Revenue Act of Charles II. (1673), in which the so-called 'vinegar beer' produced in the 'common breweries' was charged a duty of 6*d*. per barrel as against 1*s*. 3*d*. upon six-shilling beer. It is very probable that most of the vinegar first made in England was a product of the brewery which had become accidentally sour, and was then exposed to the air to complete the acetification. The manufacture of vinegar as a separate industry appears to date back not much further than the early part of the seventeenth century, and the first 'vinegar yard' in London was established about the year 1641. But long before any vinegar brewer had become established in this country 'beer vinegar' or 'alegar' was made in many a household by the simple process of adding the so-called 'vinegar plant' (*i.e* the zoogloeal form of acetic bacteria) to ale which had turned sour.

The process of making vinegar on a manufacturing scale was probably introduced into this country from France, and the methods which had been found to give the best results in the production of wine vinegar were adapted to the acetification of the English product from beer or ale. The methods of brewing used by the brewer and the vinegar maker then began to diverge, and the differences are now well marked, being based upon the different qualities desired in the alcoholic product.

Preparation of the Wort.—In preparing the fermented alcoholic liquid from malt, or malt and grain, either a mash-tun process or a conversion process is employed. The mash-tun is essentially the same as the brewer's mash-tun, with the exception that it has both rakes and sparge and is provided with a steam coil below the perforated false bottom.

The chief aim of the vinegar maker is to obtain as high a yield of alcohol as possible, and he therefore uses a malt of fairly high diastatic capacity, and makes the mash at such temperatures as will yield a wort which will attenuate well. In some works the first mash is made with water at about 65°, which gives a temperature of a little over 60° in the mash tun. After raking for an hour or two, the wort is drawn off, and a second mash made at the same temperature, and finally the 'goods' are sparged with water at about 65°-71°. In other vinegar breweries the initial mash is made with water at about 54°, and the temperature gradually raised to 65°. A second mash is made at about 65°, and the final sparging at 65°-71°. This method ensures a better yield of a more fermentable wort. It is a common practice to use raw grain, such as barley, flaked maize, or flaked rice in admixture with the malt, the diastase of the latter being sufficient to hydrolyse the whole of the starch present.

If crude rice be used a preliminary treatment, such as cooking with steam under pressure, is necessary to rupture the starch granules.

In other vinegar works the starch of the cereals used is hydrolysed by a dilute mineral acid instead of by the diastase of malt. For this purpose the grain, usually maize or rice, is mixed with dilute (about 3 p.c.) sulphuric acid in a closed iron vessel and heated for several hours by steam under pressure, until a sample of the liquid is free from unconverted starch. The contents of the converter, which now consist largely of an acid solution of dextrose, are neutralised with lime and chalk, and then drawn off, cooled, and fermented in the same way as the wort from the mash tun.

From 6 to 7 tons of grain can be treated in a converter of average size, and the whole of the starch present will be hydrolysed within 3 hours when heated with steam under a pressure of about 10 lbs.

Although most of the calcium sulphate separates from the liquid, sufficient will remain in solution to afford an indication that the vinegar was probably prepared by a conversion process.

Fermentation of the Wort.—The wort obtained by one of the above described processes is cooled in a refrigerator, and pitched with yeast as in a brewery, with the difference that a much higher temperature is permissible than in the case of beer. In fact, with some yeasts it is advisable to have a temperature as high as 21°-24° to check the growth and obtain better attenuation. If malt with good diastatic power has been used, and the wort has been prepared at a low temperature, there is usually no difficulty in attenuating a wort from a sp.gr. of 1·055 to about 1·001. In certain cases vigorous aeration of the fermenting wort is also required to effect this purpose. After fermentation, which will be complete on the third day, the *gyle* or *wash*, as it is now termed, is allowed to stand for a few days for the yeast to subside, and is then pumped into store vats until required for the further fermentation process.

Acetification of the Gyle.—The secondary or acetic fermentation of the alcoholic liquid is effected by the action of one of the species of acetic bacteria, mentioned above, which under regulated conditions of temperature and aeration oxidise the alcohol first to aldehyde and then to acetic acid, the relative proportions of the three substances present in the liquid at any given stage of the process depending largely upon the conditions of the fermentation. In addition to aldehyde and acetic acid, acetal $CH_3 \cdot CH(OC_2H_5)_2$ is also formed through the interaction of the aldehyde with the alcohol, and traces of ethyl acetate and other esters, succinic acid and other acids, are produced, their nature and quantity depending upon the nature of the substances (sugars, dextrins, &c.) in the gyle. Brown (J. Chem. Soc. 1886, 49, 172) showed that *B. xylinus* ('the vinegar plant') had the power of transforming lævulose into cellulose.

Theoretically 46 parts of alcohol should yield 60 parts of acetic acid, but in practice there is always a loss of at least 10 p.c., and in many factories very much more. This loss is due partly to volatilisation of aldehyde and esters, and partly to the fact that acetic bacteria are able to decompose the acetic acid which they have produced, and if the aeration of an acetifier is irregular the production and decomposition of acid may proceed simultaneously in different parts of the apparatus.

Should insufficient air be supplied to an acetifier, the bacteria (in this country usually Brown's *B. xylinus*) form themselves into the zoogloeal condition, which is a tough gelatinous pellicle which sooner or later chokes the acetifying medium and arrests the process. On the other hand, excess of air promotes loss by volatilisation and oxidation. The second essential is a suitable temperature for the action of the bacteria. On the Continent the acetifiers work best at a temperature of about 85° to 90° F., whereas in England the optimum temperature is 108° to 110° F., which may be partly due to acclimatisation of the bacteria. Sunlight checks the acetification process, and hence the early vinegar makers took pains to exclude all daylight from their apparatus, but under the present conditions of working this is unnecessary, for the amount of light which can find its way through the aeration holes of the large acetifiers now in use is practically negligible.

The methods of acetification first used in this country were essentially the same as those used in the earlier methods of making wine vinegar (*vide supra*), the casks being placed on their sides in a room at about 24°, or placed in rows in a 'vinegar field.' The bung holes of the casks were left open; at each end near the top holes were left for the circulation of the air. Each day a portion of the liquid was removed from a full cask and replaced by an equal quantity of liquid in a more advanced stage of fermentation, until, after about three months, the process was complete. This method of acetification, which was known as 'fielding,' has been obsolete for many years.

Quick vinegar process (*Schnellessigbereitung*). The introduction of the so-called 'quick' process of making vinegar is attributed to Schützenbach, although in its main essentials it is only a development of the method of acetification used in certain wine-vinegar factories in France in 1670 (*vide supra*). The main features introduced by Schützenbach were the use of a larger vessel, and of mechanical means for the repeated distribution of the gyle over the acetifying medium.

The acetifiers introduced into British vinegar works about sixty years ago, at the time when 'stoves,' as the acetifying rooms were called, replaced the vinegar fields, were large vats taking a charge of about 3000 gallons. About two-thirds of the way up was a perforated false bottom upon which beech shavings or twigs were loosely packed, and upon these the bacteria developed while air currents were admitted through a number of holes bored in the side of the vat just below the false bottom, and escaped through small holes in the top of the vat.

The gyle was distributed in a fine shower over the shavings, by means of a revolving sparge, and trickling downwards encountered the currents of air, which enabled the bacteria to acetify a small amount of the alcohol. The liquid from the bottom of the vat was then pumped up again, to be once more distributed over the shavings, and so on continually for two or three weeks until nearly the whole of the alcohol had been transformed into acetic acid. The drawback of shavings as a medium was that they soon became clogged with mother-of-vinegar in places, so that the air was no longer evenly distributed throughout the medium, but made channels in various places.

For this reason, in many factories shavings were replaced by basket work in superposed layers, and these worked much more regularly, and could be more easily cleaned. In other works porous lumps of charcoal, which had been washed, first with acid and then with water, were used as the acetifying medium, and promoted the acetification by the absorption of oxygen.

In Wagenmann's 'graduator,' which was devised about 1830, a perforated shelf was fixed about 5 inches from the top of the vat, and through each of the 400 holes cotton or hemp wick was suspended to guide the liquid downwards on to the shavings.

In this apparatus was foreshadowed the idea utilised in Luck's acetifier, in which the shavings were replaced by bunches of cords stretched between the distributing tray and the false bottom. This type of acetifier works regularly and is easily cleaned.

Another type of acetifier, patented by Leaker, is made up of a series of rectangular compartments containing shelves of absorbent woven material which act as the acetifying medium, whilst a fan is employed to draw the evaporated products into a condensing coil.

In Singer's acetifier several rectangular compartments are superposed, and each of them contains a series of wooden tubes packed with shavings or charcoal, and the wash is acetified as it trickles successively through these tubes from the top to the bottom of the apparatus.

Bersch's apparatus is also rectangular in form, and is packed with a series of frames filled with slats of wood with a space of about ¼ inch between each slat. These frames are superposed, with the slats running in alternate directions, and the wash is acetified as it trickles down through the successive layers of frames. It is claimed that this acetifier gives a theoretical yield of acetic acid, owing to its perfect system of aeration, but in the writer's experience, this is not the case under English methods of acetification, the best yield obtained being 0·96 p.c. of acetic acid from 0·97 p.c. of alcohol in 24 hours (J. Inst. Brewing, 1917, 23, 362).

Other modifications of the acetifier make use of a siphon within a tank for distributing the wash over a perforated tray, whilst the air required in the siphon tank is drawn from the space at the top of the acetifier, so that the aeration of the apparatus remains under control.

The working of acetifiers is liable to be disturbed by the development of vinegar eels (*Leptodera oxophila*), although these cause less trouble in this country than on the Continent, where acetification is effected at a lower temperature. Another enemy of the acetification process is the 'vinegar mite,' which, if allowed to develop, will eventually stop the process.

The use of pure cultivations of specific acetic bacteria has been shown to increase the speed of acetification and improve the flavour of the vinegar, but so far no attempt has been made to make use of them in this country, where insufficient importance is attached to the flavour of vinegar (Henneberg, Zeit. für Spiritusind. 1898, 180, and Cent. Bakt. 1905, 14, 681; Rothenbach, Woch. für Brau. 25, 445, and Deuts. Essiggind 1905, 9, 217, and Woch. fur Brau. 1906, 23, 260; Mayer, Zeit. fur Spiritusind. 21, 334; Büchner and Gaunt, Annalen, 1906, 349, 140).

The Group System.—Acetic bacteria are sensitive to the action both of alcohol and of acetic acid, being killed by alcohol of 10 p.c. strength, and weakened by alcohol of much lower strength. Their greatest vital activity is attained when the wash reaches an acidity of between 2 and 3 p.c. of acetic acid, and their acetifying power becomes less as the proportion of acid rises. It is possible, however, to acclimatise them to resist the action of more alcohol and acetic acid than under normal conditions, and on this fact is based the *group system* of acetification.

Since a 12 p.c. vinegar could not be obtained directly from one acetifier, the acetification of such concentrated products as *Essigsprit* (*vide supra*) is effected in three groups of acetifiers. The first group is charged with a wash which will yield a vinegar of about 6 p.c. strength, and this is fortified with an alcoholic wash (usually grain or potato spirit) in sufficient quantity to yield a vinegar containing 9 to 10 p.c. of acetic acid in the second group of acetifiers; and the vinegar from these is again fortified before being transferred to the third group of acetifiers for the completion of the acetification.

Filtration and Storage of Vinegar.—As soon as the vinegar has reached its maximum acidity it is at once pumped into store vats, for it is essential that it should not be left in the acetifiers, where the bacteria would oxidise the acetic acid (*vide supra*).

In some works the vinegar is clarified by the addition of potassium ferrocyanide. It has been shown by Harden that there is a possibility of hydrocyanic acid being liberated in the presence of excess of the precipitant (L. G. B. Report on Vinegar, 1908, p. 27).

After remaining in the store vats for as long a time as possible, preferably not less than three months, the crude vinegar is filtered. The filters used in most vinegar works are known as *rapes*, owing to the fact that raisin stalks were at one time—and to a limited extent are still—used as part of the filtering medium. Filter beds composed of layers of sand, shingle, and beech chips are used for the rapes in other factories, whilst in others again the rapes have been entirely superseded by filters containing paper pulp as the filtering medium.

After being filtered the 'bright' vinegar is again stored to develop an aroma through the combination of acetic acid with traces of residual alcohol, and is then diluted to the strength required by the trade.

These different strengths, technically known as 'trade numbers,' are termed Nos. 16, 18, 20, 22, and 24. It is sometimes asserted that these numbers denote the number of grains of sodium carbonate neutralised by 1 oz. of the vinegar, but both the tradition of the industry and contemporary evidence show that they indicated the price in pence per gallon at which the vinegar was sold (Penny Magazine, 1842, p. 430; Tomlinson's Cyclopædia of Useful Arts, 1854, p. 7; J. Soc. Chem. Ind. 1918, 148 R).

The trade numbers would thus originally be analogous to the term 'six ale,' meaning 'six-shilling ale.'

Before being sent out to the trade vinegar is frequently coloured to a dark shade by the addition of caramel.

Distilled Vinegar.—In the early method of preparing *aromatic* or *radical vinegar* (*vide supra*), vinegar was distilled in a retort at the ordinary pressure, but in the modern process the distillation is effected at a lower temperature under reduced pressure, and can thus be carried very much further without risk of burning the solid residue, and flavouring the distillate.

The small stills commonly used for this purpose are made of gunmetal lined with tin, and are heated by a steam jacket. The outlet pipe from the still is connected with a tin coil immersed in a vessel of running water, and delivers into a receiver in which is a pipe connected with a vacuum pump. The still takes a charge of about 100 gallons, which is distilled under a reduced pressure of about 20 inches until only a semi-solid mass resembling treacle remains in the still.

The distillate is sold under the names of *distilled malt vinegar, white vinegar* and (incorrectly) *white wine vinegar.*

In addition to wine and malt, vinegar is prepared from many other substances. *Cider vinegar* is of a yellowish colour, sp.gr. 1·013 to 1·015. It contains 3½ to 6 p.c. acetic acid, and on evaporation leaves a mucilaginous residue, smelling and tasting of baked apples, and containing malic but not tartaric acid. The residue varies from 1·5 to 1·8 p.c. Genuine cider vinegar is distinguished from spurious cider vinegar by the residue, which consists of glycerol, albuminous matters, gums, malic and other organic acids and mineral matters. They have no rotation and little cupric reducing power after the usual clarification with basic lead acetate solution. Acetylmethyl carbinol is a characteristic constituent of cider vinegar. The ash of a pure cider vinegar amounts to not less than 0·25 p c., consisting mainly of potassium oxide, with small quantities of alumina, lime, magnesia, sulphate, and phosphate, variable amounts of carbonate, and complete absence of soda. Spurious cider vinegars leave a molasses-like residue and an ash with a large percentage of lime or soda (Doolittle and Hess. *See* also Smith, J. Amer. Chem. Soc. 1898, 20, 3; Leach and Lythgoe, *l.c.* 1904, 26, 375; Van Slyke, New York Agric. Exp. Stn. Bull. 1904, 258, 439; Ladd, N. Dakota Exp. Stn. Bull. 32, 278). Cider vinegar made by the 'quick' process contains on the average 5·7 p.c. of acetic acid, and 0·4 p.c. of alcohol. The total solids, ash and glycerol are substantially the same as in the cider from which the vinegar was prepared (Tolman and Goodnow, J. Ind Eng. Chem. 1913, 5, 928). *Perry* and *crab-apple vinegar* are used in Wales and Monmouthshire, and possess characteristic properties.

Glucose or *sugar vinegar* is prepared by the conversion of amylaceous substances into sugar, by the action of dilute acids, followed by fermentation and acetification. It contains dextrose, dextrin, and very often gypsum, with hardly any proteins. The ash is composed mainly of potassium salts, is rich in sulphates, and in the case of cane-sugar vinegars, readily fusible (Allen's Comm. Org. Anal. 1909, 498). It is stated to be used for adulterating wine vinegar. It can be distinguished from other vinegars by the addition of 3 or 4 volumes strong alcohol, which produces a slimy precipitate of dextrin. Barium chloride usually gives a copious precipitate, due to the sulphuric acid used in the manufacture of the glucose.

Vinegar is now made from skim milk by addition of sugar, neutralisation with chalk, pitching first with yeast and then with *Mycoderma aceti* (Barbier, Fr. Pat. 334071, 1903).

Date vinegar is made by the consecutive alcoholic and acetic fermentations. Compared with malt vinegar, it is low in phosphoric aci and nitrogen.

Wood 'vinegar,' as its name indicates, i nothing more than dilute acetic acid coloure with caramel, and sometimes flavoured wit brewed vinegar or with acetic ester. It cor tains about 0·2 to 0·6 p.c. of total solids, 0·02 t 0·04 p.c. of ash, and traces of phosphoric aci and nitrogen.

Properties.—Malt vinegar is a brown liquid of a characteristic odour due to the presence, in addition to the acetic acid, of acetic and other esters. Acetic ester is sometimes added in small quantity to increase this aroma.

The addition of 1 part sulphuric acid to 1000 parts vinegar was permitted by an Excise Act of George III. of 1818, but this Act has long been repealed. Such addition is quite unnecessary, and is probably never made at the present time.

Malt vinegar usually contains alcohol, dextrin, sugar, and extractive matter, acetates, chlorides, and sulphates, and on evaporation and ignition leaves a residue containing much phosphate.

Analysis of typical vinegars sold as 'malt vinegar' are given in the table at top of p. 22.

Of these samples Nos. I. and II. show the normal figures for barley malt vinegar. No. III. was said to contain products of cereals other than barley, whilst No. IV. was made from a mixture of rice and green malt, the former being responsible for the low phosphoric acid, and the latter for the high nitrogen. No. V. contains abnormally low solid matter, and No. VI. was made by the conversion process.

Wine vinegar varies in colour from pale yellow to red; that made from white wine is most esteemed; it usually has an alcoholic odour. Its sp.gr. is 1·014 to 1·015; it contains from 6 to 12 p.c. acetic acid. A litre (1·76 pint) of Orleans vinegar usually saturates 6 or 7 grams (92 to 108 grains) of pure dry sodium

No.	Sp gr. at 15 5°.	Acetic acid.	Total solids.	Ash.	P_2O_5.	Nitrogen.	P_2O_5 on original solids.	Nitrogen on original solids.
		p c.	p c.	p.c.	p c.	p c.	p c.	p c.
I.	1017·5	5·4	2·74	0·49	0·07	0·07	0·69	0·64
II.	1021	5·4	3·84	0·39	0·13	0·14	1·08	1·23
III.	1014·5	5·1	1·68	0·16	0·03	0·03	0·32	0·28
IV.	1021	5·9	3·67	0·34	0·04	0·14	0·34	1·11
V.	1013	4·5	1·75	0·24	0·09	0·08	1·00	0 90
VI.	1014	4·3	2·04	0·47	0·07	0·06	0·83	0·70

carbonate. On evaporation the total extract varies from 1·7 to 2·4 p.c., of which 0·25 p.c. is usually potassium tartrate, a salt peculiar to wine vinegar. The residue, with the exception of the tartar, should dissolve in alcohol.

The proof vinegars of various countries differ considerably; the minimum of acetic acid allowed by the various Pharmacopœias is—France, 8 to 9 p.c.; Germany and Austria, 6 p.c.; Belgium, 5 6 p.c.; Russia, 5 p.c.; United States, 4·6 p.c. Vinegar is no longer official in the British Pharmacopœia. The bulk of the vinegar sold in this country is of a strength just over 4 p.c. A standard was fixed by the Society of Public Analysts in 1876 of a minimum of 3 p.c., and this being accepted by the trade, became in practice the legal standard. In 1912 the Local Government Board recommended the adoption of a 4 p.c. standard, but no statutory force has been given to this recommendation.

Analysis of Vinegar.

Acidity.—This is usually estimated by titration with standard alkali, with phenolphthalein as indicator. In the case of dark samples caramel may be precipitated by means of fuller's earth and an aliquot part of the filtrate titrated. 'Spotting' tests with litmus as indicator give results about 1 p.c. lower in terms of *N*/2 alkali solution than direct titration with phenolphthalein as indicator (Brode and Lange, Arb. Kaiserl. Gesundheitsamte, 1909, 30, 1).

Total solids.—A measured quantity is evaporated and the residue dried to constant weight at 100°. Constant shaking during the evaporation is necessary to expel the acetic acid, and a final titration of the acidity of the residue is advisable.

Alkalinity of the ash.—This may afford an indication of the probable origin of the vinegar, a glucose product, for instance, showing a low proportion of potassium oxide owing to the mineral acid used for the hydrolysis having combined with part of the bases. Variations in the results given by different types of vinegar are seen in the following results:—

	Vinegar from grain and malt.	Grain and sugar	Rice.	Sugar.
Alkalinity at K_2O per 100 parts of vinegar	0·091–0·118	0·03	0·013	trace

(Allen, Analyst, 1894, 19, 15).

Free mineral acids.—These are seldom, if ever, added to vinegar at the present time. They may be detected by means of 0·1 p.c. methyl violet solution, which is not affected by acetic acid, but is changed to blue or green by mineral acids (Hilger, Arch. Pharm. 1876, 193). A method of detecting and estimating free sulphuric and other acids was based by Hehner on the fact that vinegars containing acetates or tartrates cannot contain free mineral acid, and since on igniting these salts they are decomposed into carbonates, an examination of the ash of the vinegar will afford an indication of the presence of free acid (Analyst, 1877, 1, 105). A later method devised by Richardson and Bowen (J. Soc. Chem. Ind. 1906, 25, 836) enables an estimate to be made of the amount of sulphuric acid originally added to a vinegar.

Combined sulphuric acid. — Commercial samples usually contain from about 0 03 to 0·17 p.c. of sulphuric acid in the form of sulphates, quantities in excess of the lower figure usually being due to the vinegars having been made by the conversion process.

Added acetic acid.—No direct test for added acetic acid has been devised, and an inference is usually drawn from the deviation of the figures from those normally given by a vinegar brewed from barley malt. Fincke's test for formic acid, which is usually present in acetic acid (*vide supra*), is untrustworthy, since formic acid is also a normal constituent of grain and wine vinegars.

Phosphoric acid.—The ash from 10 c.c. of the vinegar is dissolved in dilute nitric acid, and treated with a large excess of molybdic reagent. The yellow precipitate is washed twice by decantation with cold water, dissolved in ammonia solution, and the solution evaporated. The weight of the residue multiplied by 28·5 gives the amount of phosphoric acid P_2O_5.

Nitrogen is conveniently estimated by Kjeldahl's method in 10 to 25 c.c. of the vinegar. For comparing the results both of phosphoric acid and nitrogen in vinegars of different strength Hehner's method of expressing them in terms of 'original solids' is a convenient though empirical, method (Analyst, 1891, 16, 92; *ibid.* 1893, 18, 245).

Optical Standard for Malt Vinegar.—The U.S.A. Dept. Agric. (Circular No. 19, 1906) stated that vinegar made from barley malt or cereal was dextrorotatory, but Chapman (Analyst, 1912, 37, 123) showed that the proteins and their hydrolytic products may cause a vinegar to show a lævo-rotation.

Caramel.—Added caramel may frequently be precipitated by the addition of fuller's earth, but the test is not always satisfactory, since the amount removed varies with the character of the earth (Dubois, J. Amer. Chem. Soc. 1907, 29, 75). A method of precipitation with tannin is recommended by Lichthardt (J. Ind. Eng. Chem. 1910, 2, 389), but has the drawback that proteins and iron are also precipitated by tannin. Amthor has based a method of detecting caramel on its precipitation by paraldehyde (Zeitsch. anal. Chem. 24, 30).

Metallic Impurities.—The chief metallic impurities to be looked for in vinegar are iron, copper, lead, and tin. The presence of iron may be detected by adding potassium ferrocyanide directly to the vinegar. For the detection of traces of the other metals the methods (suitably modified) described under AERATED WATERS may be used, whilst arsenic may be detected and estimated by the official method of the Conjoint Committee of the Soc. Chem. Ind. and Soc. Public Analysts (Analyst, 1902, 27, 48).

Formic acid in distilled vinegar or spirit vinegar may be estimated by the method recommended by Ost and Klein (Chem. Zeit. 1908, 32, 815). The acid is neutralised with alkali and titrated with permanganate. Other substances which reduce permanganate must be absent, which renders the method inapplicable to ordinary malt and grain vinegars.

Oxalic acid may be estimated by concentrating the vinegar and then boiling with calcium acetate solution.

Potassium hydrogen tartrate is estimated by titration against $N/2$ alkali, and tartaric acid by conversion to potassium hydrogen tartrate and subsequent titration (Zeitsch. anal. Chem. 1908, 47, 57).

(For the estimation of methyl alcohol in vinegar, *see* Ann. Chim. anal. 1901, 6, 127 and 171.)

Cayenne pepper, ginger, and other flavouring matters may be discovered by neutralising and tasting the vinegar.

Chevallier has found fuchsine in French wine vinegars. C. A. M.

METALLIC ACETATES.

Aluminium acetates.

The triacetate or normal acetate $Al_2(C_2H_3O_2)_6$ is not known. A solution corresponding to this compound, but which appears to be a mixture of the diacetate and acetic acid, is the only acetate of commercial importance. It is known as 'red liquor' or 'mordant rouge,' and is largely used in dyeing and calico-printing, especially for the production of red colours, madder reds and pinks (whence its name of red liquor); for the production of dense lakes, and for waterproofing woollen fabrics. It is prepared by several methods

A solution of alum is added to acetate of lime liquor. The lime is precipitated as sulphate, its place being taken by the aluminium, with the formation of aluminium acetate; ammonium or potassium sulphate (according to whether ammonium or potassium alum has been used) is produced at the same time. The mixture is agitated and allowed to settle, and a small quantity of the clear fluid removed and tested by the addition of alum; if a precipitate forms sufficient alum has not been used and more must be added. The solution is filtered, concentrated to a specific gravity of 1·087 to 1·10, and allowed to deposit any calcium sulphate still present. Calcium sulphate, being slightly soluble in water, is contained in the liquid in small quantity, and diminishes the brilliancy of the colours produced. By the substitution of lead acetate for the calcium acetate a better product is obtained. For this purpose 100 lbs. alum are dissolved in 50 gallons water, and treated with 100 lbs. finely-powdered lead acetate with constant stirring; or, using the same quantities, 10 lbs. crystallised sodium carbonate are added before the acetate of lead; or, to 100 lbs. alum in 50 gallons water 6 lbs. of carbonate are added in small portions, followed by 50 lbs. of lead acetate. The addition of the carbonate is made with a view to the production of a basic aluminium sulphate in addition to the acetate, and as the sulphate assists the mordanting, less acetate is required. The solutions are allowed to settle and decanted. They contain the aluminium acetate mixed with basic aluminium sulphate and alkaline sulphate.

An aluminium sulpho-acetate appears to act satisfactorily. It is prepared by mixing (1) 453 lbs. ammonium alum (or 383 lbs. aluminium sulphate), 379 lbs. lead acetate, 1132 lbs. water; or (2) 453 lbs. alum (or 333 lbs. aluminium sulphate) and 158 lbs. acetate of lime. The mixture is agitated, settled, and the clear liquid decanted.

By the use of aluminium sulphate, red liquor of the same density contains much more of the active alumina than that prepared with alum. Thus in a sample of the former 1 gallon contained 4 oz. 416 grs. alumina, whilst the average amount found in three samples prepared from alum was 3 oz. 245 grs. The addition of a little ammonia or other alkali to the red liquor prepared from aluminium sulphate is advantageous for certain colours. Red liquor usually contains from 3 to 5 p.c. alumina (Al_2O_3) and 6 to 10 p.c. acetic acid; its density varies from 1·085 to 1·120.

The importance of the formation of the gelatinous basic aluminium acetate $Al(O{\cdot}COCH_3)OH$ in protecting aluminium plant from the action of acetic acid has been mentioned above.

Ammonium acetate $C_2H_3O_2NH_4$.

The crystalline salt is usually prepared by saturating glacial acetic acid with dry ammonia gas. In solution it may be prepared more cheaply by neutralising acetic acid solution with ammonia. On evaporation, a solution of the salt loses ammonia, and leaves the acid acetate or diacetate.

Ordinary solid ammonium acetate always has an odour of acetic acid; it is very soluble in water and alcohol.

Pure ammonium acetate should be entirely volatilised on heating. The commercial salt usually contains the same impurities as sodium acetate.

The official ammonium acetate solution of the B.P. is prepared by neutralising 33 p.c. acetic acid with ammonium carbonate and diluting the liquid to a sp.gr. of 1·016. When treated with an equal volume of a saturated solution of hydrogen sulphide it should not darken in colour (limit of heavy metals).

Calcium acetate. *Diacetate of lime. Pyrolignite of lime.* $Ca(C_2H_3O_2)_2$.

This important salt is prepared by neutralising acetic acid, or pyroligneous acid, with lime or chalk.

In the preparation from pyroligneous acid, the crude acid may be used, in which case the acetate of lime is known as *brown acetate*; or the distilled liquor may be employed, producing *grey acetate*. The acid is placed in large wooden or iron pans, and powdered chalk or lime added in slight excess; the liquor remains at rest at a warm temperature until clear, and is then siphoned off into the evaporating pans. It is generally evaporated by means of coils of pipe through which steam passes; in this case the vessels are usually wooden, and lined with lead, but sometimes iron pans are used, the evaporation being conducted over a fire. The tarry impurities which rise to the surface as the liquid evaporates are removed with a skimmer. As the acetate forms, it is withdrawn and drained in wicker baskets suspended over the pans.

The proper drying of the salt is necessary to the formation of a good product. In large works a drying house is used, which is usually a wind furnace 7 or 8 feet long, 4½ feet broad. It is first heated from 75° to 115°, and the fire slackened; the salt is then spread over the bottom to the depth of about 2 inches, and when somewhat dry an equal quantity is spread above it, the salt is repeatedly turned, and the heat continued for about 24 hours. When the product appears to be dry, the heat is increased to about 125°, and the last traces of moisture driven off. Care must be taken that the heat is not too high, or the salt becomes decomposed. As in the case of sodium acetate, no sparks must touch the mass, or it may burn away like tinder.

The product, when prepared from the *brown* liquor, is dark-coloured and contains charcoal and decomposed tarry matters; it may be dissolved in 3 parts hot water, filtered through animal charcoal, and again evaporated and crystallised, yielding a nearly colourless product.

Pure calcium acetate crystallises in silky needles or prisms containing two molecules of water. At the ordinary temperature the crystals effloresce, and at 100° become anhydrous, forming a white powder of saline taste, very soluble in water.

Calcium acetate is used in the preparation of other acetates, and of acetic acid, and in calico-printing. The pure salt is completely soluble in water and proof spirit. The commercial article usually contains 62 to 67 p.c. of real acetate, and 1 to 8 p.c. of matters insoluble in water. The impurities are hydroxide, carbonate, and sulphate of calcium and tarry matters; formate and other salts of calcium with fatty acids also occur.

Many methods of assay for this substance are in use, varying considerably in accuracy.

The most trustworthy method is to distil with pure phosphoric acid and titrate the distillate as already described under acetic acid (*see* Stillwell, J. Soc. Chem. Ind. 1904, 305; Grosvenor, *ibid.* 530; Gladding, J. Ind. Eng. Chem. 1909, 250). The acetic acid may also be expelled by evaporation with formic acid (Heermann, Chem. Zeit. 1915, 39, 124).

Calcium aceto-chloride $CaC_2H_3O_2Cl,5H_2O$ has already been described as used in Condy's process for the preparation of pure acetic acid.

Copper acetates.

The normal *copper acetate* is prepared by dissolving cupric oxide or verdigris in acetic acid; or by the action of copper sulphate on the acetates of lead, calcium, or barium.

It crystallises in prisms; soluble in 13 parts cold or 5 parts hot water, and in 14 parts alcohol. In commerce it usually occurs in bunches of deep-green coloured opaque crystals known as 'grappes.'

Copper acetate is used in the manufacture of pigments; as an oxidising agent in the indigo vat; and, formerly, for the preparation of acetic acid.

Basic copper acetate. *Verdigris. Vert-de-gris Vert de Montpellier. Grunspan.*

This substance consists of a mixture of mono-, di-, and tri-basic acetates of copper, which are present in different proportions in different varieties of verdigris.

At Grenoble and Montpellier the following process is used: The 'marcs' or residues from the wine factories, consisting of the skins and stems of grapes, are loosely placed in earthen vessels, about 16 inches high, 14 inches in diameter at the widest part, and 12 inches at the mouth, covered and allowed to ferment, until on inserting a piece of copper (previously moistened with verdigris and dried), it becomes uniformly coated green in 24 hours. The fermentation should not proceed too far, or decomposition may ensue.

The copper used is in sheets $\frac{1}{24}$ inch thick, 4 to 6 inches long, and 3 to 4 broad, each weighing about 4 oz.; they are freed from scales, if necessary, rubbed with a solution of verdigris and dried; unless this precaution be adopted, the first coating produced by the marcs will be black instead of green. They are heated over a charcoal fire until as hot as the hand can bear, and placed in an earthenware vessel in layers with the marcs. 30 to 40 lbs. of copper are used for each vessel. In from ten to twenty days, according to the temperature, the covers are removed, when, if the process has progressed favourably, the marcs will be whitish and the copper covered with fine, glossy, green crystals. The plates are then removed and placed on end one against another. After two or three days they are moistened by immersion in water or damaged wine, and again placed on end for about a week. This alternate moistening and exposure to the air is continued for about six or eight weeks. The plates thus become covered with increasing coatings of the verdigris, which is detached and the plates are again used until entirely eaten away. The verdigris is kneaded with a little water into leather bags, pressed into rectangular cakes and dried.

This substance is known as *blue verdigris*, and consists principally of the basic acetate

$$(C_2H_3O_2)_2Cu_2O.$$

It should be dry, of a fine bluish colour, and soluble in dilute acids and ammonia.

Green verdigris contains as a principal constituent the sesquibasic acetate, $CuO{\cdot}2Cu(C_2H_3O_2)_2$, and is prepared by placing the copper plates alternately with cloths moistened every two or three days with pyroligneous acid or acetic acid until the plates show green crystals. The plates are arranged so as to allow free access of air and occasionally moistened, for five or six weeks. Large quantities of verdigris are manufactured in England by this process from pyroligneous acid. The imports of verdigris are very small.

In Abresh's process (Fr. Pat. 391603, 1908) minerals containing the oxide or carbonate of copper are decomposed with 15 p.c. acetic acid solution, the excess of acid neutralised or distilled, alkali added to precipitate iron aluminium, calcium, &c., the liquid filtered and concentrated, and the copper acetate separated by crystallisation.

The various forms of verdigris are used as oil and water colours. With white lead it is used in Russia and Holland as an oil paint, which by double decomposition produces a peculiar green. The paint is considered a good preservative. Verdigris is used in dyeing and calico-printing, and for the preparation of Schweinfurth green and other copper paints.

Verdigris is frequently adulterated with chalk, sand, clay, pumice, and sulphates of copper, barium, and calcium. When brass sheets have been used in the preparation instead of copper, zinc will also be present.

When warmed with dilute hydrochloric acid the sand, clay, baryta, &c., will remain undissolved, and may be weighed. The total residue in a good sample will usually amount to 3 p.c., but should not exceed 6 p.c.

Aceto-arsenite of copper. *Schweinfurth green* (*v.* ARSENIC).

Ferric acetate $Fe_2(C_2H_3O_2)_6$. This salt is prepared by the addition of calcium or lead acetate to ferric sulphate or iron alum, avoiding excess of the acetate. It is used as a mordant, its action corresponding with that of aluminium acetate. An alcoholic solution is used in medicine, but is no longer an official drug in the B.P.

For many purposes a mixture of ferrous and ferric acetates is preferred. It is prepared by repeatedly pouring pyroligneous acid on iron turnings until saturated with iron. The liquid is known as 'pyrolignite of iron,' 'bouillon noir,' 'liqueur de ferraille.'

Ferrous acetate $Fe(C_2H_3O_2)_2$. *Pyrolignite of iron; iron liquor or black liquor.* Is prepared on the large scale by the action of crude pyroligneous acid of sp.gr. 1·035 to 1·040 on iron turnings, nails, &c., at a temperature of 65°. The solution is frequently agitated and the tarry matters skimmed from the surface as they rise.

It is found that the purified acid produces a less satisfactory liquor, a fact due, according to Moyret (J. Soc. Dyers, i. 117), to the presence of a small quantity of pyrocatechol in the crude acid, which forms a compound with the ferrosoferric oxide in the solution, and causes its intense colour and keeping properties.

The liquid is intensely black, of sp.gr. 1·085 to 1·090, and is evaporated until its density rises to 1·120, or sometimes to 1·140. It is then ready for use, and is known as 'printer's iron liquor.' The liquor of density 1·120 contains about 10 p.c. iron.

The density of the liquor used by dyers is frequently raised by the addition of copperas (ferrous sulphate); thus, the addition to 1 gallon of black liquor, sp.gr. 1·085, of ½ lb. copperas, would raise its density to 1·111. Tannin also is sometimes added.

Black liquor is also prepared by the action of ferrous sulphate on acetate of lime; the liquor produced has an average density of 1·11, and always contains calcium sulphate. By the action of lead acetate on ferrous carbonate, carbonate of lead and ferrous acetate are produced.

Black liquor absorbs oxygen from the air, forming ferric acetate, which is always present in the liquid. To diminish this action clean metallic iron is frequently added.

It is largely used in calico-printing and in dyeing, in the preparation of blue, violet, black, brown, and other colours, and for producing a black colour on hats, furs, leather, wood, &c.

Lead acetate. *Normal or di-acetate of lead. Sugar of lead. Sel de Saturne. Bleizucker.* $Pb(C_2H_3O_2)_2$.

For the preparation of *white acetate* of lead, leaden vessels are used, or copper pans, on the bottom of each of which a piece of metallic lead is soldered to produce a galvanic action and prevent the copper from being acted upon. In the vessel acetic acid of 45 p.c. or less is placed, and to 100 parts of 45 p.c., or a proportionate quantity of a weaker acid, 86·5 parts of litharge are added in small quantities, with constant stirring, until the liquid is nearly neutral; it is then heated to boiling and impurities skimmed from the surface, transferred to another vessel, evaporated to a density of 1·5, and removed to the crystallising pans, which are usually of wood, lined with lead or copper, 4 feet by 2 feet, and 6 or 8 inches high. The coarsely crystalline mass thus obtained is drained on wooden racks, and broken into lumps for the market.

A coarser variety, known as *brown acetate*, is prepared by substituting distilled pyroligneous acid for the purer acid. The muddy liquid produced is left to settle in a large tun, and the supernatant liquid transferred to a large iron pan and heated to boiling. It is again allowed to settle, transferred to another pan, evaporated until crystallisation commences, when about 3 volumes of water added, causing the remaining impurities to rise to the surface. The liquid is skimmed and diluted if the liquid is not sufficiently clear, and again evaporated until a small portion crystallises when removed and cooled. It is then ladled into pans and allowed to crystallise.

As a rule, about 3 parts acetate are produced from 2 parts litharge.

By another method granulated lead, white lead residues, &c., are placed in vessels standing obliquely one above another; the upper vessel is filled with strong acetic acid, which after the expiration of half an hour is allowed to run into the second vessel. Every half-hour it is removed to a lower one. After the acid has been removed, the lead absorbs oxygen rapidly, and becomes heated. On leaving the last vessel, the acid is again passed through the series, dissolving the acetate which has been formed, and is evaporated and crystallised.

Schmidt (Eng. Pat. 7192, 1897) describes a process for preparing the neutral and basic acetates of metals such as lead and copper by the action of dilute acetic acid and oxygen upon the metal contained in closed iron cylinders.

Pure lead acetate is a white crystalline salt of sweetish taste and weak acid reaction, containing 3 molecules of water. 100 parts of water dissolve 54·38 parts at 25°, 87·77 parts at 35°, and 154·25 parts at 45°. At 280° it melts, and when heated more strongly it forms a basic salt and suddenly solidifies.

Lead acetate is largely used in dyeing and calico-printing; for the preparation of alum mordants, &c.; in the manufacture of chrome yellow and other pigments, and in medicine.

Lead forms two well-defined basic acetates—the dibasic acetate $Pb(C_2H_3O_2)_2PbO,2H_2O$ (Wittstein, Annalen, 52, 253), formed by dissolving litharge in the normal acetate in calculated proportions; and the tribasic acetate $Pb(C_2H_3O_2)_2,2PbO$·aq, prepared by boiling the normal acetate with excess of litharge for some time. Lead acetate and solutions of subacetate of lead are official drugs of the B.P. The solutions are termed *Goulard water* and *Liquor plumbi subacetatis*.

In 1911 the annual production of *white acetate* in Germany was estimated at 2600 metric tons, about half of which was exported, mainly to Great Britain (Badermann, Zeitsch. angew. Chem. 1911, 24, 1211).

Lead sub-acetate $CH_3·CO_2Pb$ may be obtained by the action of acetic anhydride on lead suboxide at 195°. It is a bluish grey substance, soluble in alcohol (Denham, Chem. Soc. Trans. 1919, 109).

Magnesium acetate. A basic acetate of magnesium, prepared by warming the normal acetate with magnesia, is stated to be a powerful antiseptic, disinfectant, and deodoriser (W. Kubel, Ber. 15, 684–686). A syrupy solution of the salt containing suspended magnesium hydroxide is found in commerce under the name of 'Sinodor.'

Potassium acetate $C_2H_3O_2K$ occurs in the sap of many plants, and of trees.

Its mode of preparation is similar to that of sodium acetate. It is a deliquescent crystalline solid, soluble in 0·53 part ice-cold water, and in hot water forms a solution which, boiling at 169°, contains 88 p.c. of the salt.

When chlorine gas is passed through a solution of potassium acetate, carbon dioxide is evolved and a powerful, unstable, bleaching fluid is produced.

Potassium acetate may contain the same impurities as the sodium salt. The di- and triacetates are prepared like those of sodium.

Sodium acetate $C_2H_3O_2Na$ is formed (1) by the action of dilute acetic acid on sodium carbonate, the solution being evaporated and crystallised; (2) by neutralisation of pyroligneous acid with soda, and evaporation and fusion of the salt to remove tarry matters; (3) by the addition of Glauber's salt to solution of acetate of lime or of lead. The solution is decanted and filtered from the precipitated calcium or lead sulphate, evaporated and crystallised, and the crystals dissolved and recrystallised. Methods (2) and (3) are used on the manufacturing scale.

Sodium acetate forms monoclinic crystals, containing 3 molecules of water; has a strong saline taste; is soluble in 2·8 parts cold water and in 0·5 boiling water. The crystals melt completely at 75° and lose their water of crystallisation at 100°. By solution of this salt in ordinary strong acetic acid and rapid evaporation the diacetate of soda is formed; when glacial acid is used the triacetate is produced.

Sodium acetate is used for the preparation of acetic acid and in medicine, but is not official in the B.P.; for the preservation of meat and other foods instead of salt. The saturated solution is occasionally used for filling carriage foot-warmers.

The commercial acetate is liable to contain sulphates, chlorides and carbonates, and metallic salts. Tarry matters are frequently present from the pyroligneous acid used in its manufacture. Acetate of lime, and sulphate and carbonate of potassium are occasionally added as adulterants.

For the estimation of acetic acid in commercial acetates the method of Stillwell and Gladding in a modified form is used (*v. supra*).

Titanium acetate. A double acetate of titanium has been patented by Kunheim (Ger. Pat. 248251, 1911). It is prepared by adding excess of an alkali solution to a strong solution of a salt of trivalent titanium, and crystallising the double salt in a vessel from which air is excluded.

Anhydrous metallic acetates may be obtained by the action of acetic anhydride on nitrates containing water of crystallisation. The reaction is accelerated catalytically by acids and also apparently by water, as anhydrous nitrates do not react so readily (Spath, Monatsh. 1912, 33, 235).

ALKYL ACETATES. *Acetic esters.*

Acetic acid forms numerous acetates with organic radicals. Some of these occur in the oils from various seeds.

Amyl acetates $C_5H_{11}(C_2H_3O_2)$.

The following isomeric amyl acetates are known:—

1. Normal amyl acetate, boiling at 147·6° (Gartenmeister); at 148·4° (737 mm.) (Lieben and Rossi).
2. *Iso*amyl acetate.
3. Methyl propyl carbinyl acetate, boiling at 133°–135° (Wurtz); at 134°–137° (Schorlemmer).
4. Methyl *iso*propyl carbinyl acetate, boiling at 125° (Wurtz).
5. Diethyl carbinyl acetate, boiling at 132° (741 mm.) (Wagner and Saytzeff).
6. Tertiary amyl acetate, boiling at 124° (750 mm.) (Flavitzky).

Of these, only the second is of technical interest.

***iso*Amyl acetate**, generally known as *amyl acetate* $(CH_3)_2CH·CH_2CH_2O·C_2H_3O$, is a colourless liquid with an odour resembling that of jargonelle pears. Sp.gr. 0·8762 15°/4° (Mendeléeff), 0·8562 22°/4° (Bruhl), b.p. 138·5°–139° at 758·6 (Schiff).

It may be prepared by distilling a mixture of 1 part amyl alcohol, 1 part strong sulphuric acid, and 2 parts dried potassium acetate; or by warming a mixture of 1 part amyl alcohol, 1 part acetic acid and 0·5 part strong sulphuric acid on the water-bath and pouring the solution when cold into excess of water. The upper layer of purified amyl acetate is separated, shaken with a strong solution of sodium carbonate, again separated, dried over calcium chloride, and redistilled.

It may be prepared commercially from fusel oil, hydrochloric acid, and calcium acetate (Wilson, Eng. Pat.), and by the interaction of chloropentane with sodium acetate, in the presence of strong acetic acid. To prevent the formation of amylene the sodium acetate should be in a porous, bulky condition (Kaufler, Eng. Pat. 2779, 1913). The commercial amyl acetate contains some of the other isomerides.

It is insoluble in water, but dissolves in all proportions in ether, amyl alcohol, and ordinary alcohol. The latter solution is largely used under the name of *Jargonelle pear essence* for flavouring confectionery.

Camphor, tannin, resins, &c., dissolve readily in amyl acetate. A solution of gun-cotton therein is used as a varnish, for lacquering metals, &c., and in the form of a stiff jelly, mixed with opaque substances such as china clay, as a substitute for celluloid.

It is also used in the manufacture of photographic films and in some smokeless powders.

It has been recommended for use for the production of a standard flame in photometry (J. Soc. Chem. Ind. 1885, 262).

The Hefner standard lamp burns amyl acetate as an illuminant.

Ethyl acetate. *Acetic ether* $C_2H_5(C_2H_3O_2)$ is a fragrant limpid liquid of sp.gr. 0·92454 0°/4°. b.p. 77·15° (Wade and Merriman); sp.gr. 0·92446 0°/4°, b.p. 77·17° at 760 mm. (Young and Forty).

For the preparation of acetic ether 3·6 pts. by weight of commercial absolute alcohol are mixed with 9 pts. sulphuric acid with constant stirring. After standing twenty-four hours the mixture is poured on 6 pts. of fused sodium acetate (in small lumps), allowed to stand for twelve hours and distilled. The product is rectified over calcium chloride and potassium carbonate and redistilled.

Clark recommends the following process: 283 c.c. (10 oz.) of rectified alcohol (sp gr. 0·838) are placed in a flask, and 283 c.c. of sulphuric acid (B.P.) are added with constant stirring. The liquid should be cooled externally as far as possible, allowed to stand till the temperature has sunk to 15°, and 351 grams (12⅜ oz.) of dried sodium acetate added gradually, with constant stirring and cooling. The liquid is distilled until 400 c.c. (14 oz.) have passed over; this is digested for three days with 2 oz. freshly dried potassium carbonate and filtered. The filtrate is distilled on the water-bath until all but 1 oz. has passed over. On the large scale dried sodium acetate may be substituted for the potassium carbonate with advantage (*v.* further W. I. Clark, Pharm. J. [3] 1883, 777).

Ethyl acetate may be prepared by the action of an aluminium alkyl oxide on acetaldehyde in the presence of aluminium chloride, which has preferably been added during the preparation of the alkyl oxide from aluminium and alcohol; or the melted alcoholate may be dissolved in anhydrous camphor, alum, &c., to increase the catalytic action (Consortium f. Elektrochem. Ind., Ger. Pat. 286812, 1914; Eng. Pat. 4887, 1915).

In the process of Farbwerke vorm. Meister, Lucius and Bruning (Eng. Pat. 1288, 1915) acetaldehyde is treated with a filtered solution of aluminium ethoxide in an organic solvent, such as xylene or solvent naphtha at 0°-15°, a yield of about 86 p.c. of the theoretical amount of ethyl acetate being claimed (*cf.* Senderens and Aboulenc, Compt. rend. 1911, 152, 1671; Kuitenacker and Habermann, J. pr. Chem. 1911 [ii.] 83, 541).

Ethyl acetate is soluble in 8 parts of water at 0°, and somewhat *less* soluble in water at 15°. On the other hand, 1 part water dissolves 26 parts of the acetate at 0° and 24 parts at 15°.

Commercial acetic ether usually contains less than 75 p.c. of ethyl acetate, the rest being acetic acid, alcohol, water, ether, &c. It occurs, together with other organic acetates, in vinegar and wines.

Methyl acetate $CH_3(C_2H_3O_2)$ is a colourless fragrant liquid of sp.gr. 0·9398 15°/15°, boiling at 57·5° (760 mm.) (Perkin). It occurs in wood-spirit, and in crude wood-vinegar.

Methyl acetate is best prepared by distilling a mixture of 1 part methyl alcohol, 1 part potassium acetate, and 2 parts sulphuric acid. The product is dried over calcium chloride and quicklime and redistilled. It is soluble in water, alcohol, and ether.

A solvent for resins, fats, cellulose, nitrate, &c., which consists largely of methyl acetate, may be prepared by distilling pyroligneous acid until a tenth of its volume has passed over, then adding a mineral acid, and continuing the distillation until a third of the residue has distilled. The united distillates are then rectified (Heilbronner and Criquebeuf, Fr. Pat. 464646, 1913).

ACETIC ANHYDRIDE $(CH_3CO)_2O$ is formed smoothly and quantitatively by heating acetyl chloride with a metallic acetate. It is not, however, necessary to make a separate preparation of the acetyl chloride and almost any reaction which yields acetyl chloride will yield acetic anhydride if an excess of metallic acetate be employed. The method originally employed by Gerhardt (Ann. Chim. Phys. 1853, [3] 37 285) consisted in treating an excess of anhydrous potassium or sodium acetate with a chloride or oxychloride of phosphorus. Later, Geuther (Annalen, 1862, 123, 114) showed that the reaction occurs according to the equation

$$4CH_3COONa+POCl_3 = 2(CH_3CO)_2O+3NaCl+NaPO_3$$

This method is a satisfactory one, but since acetic anhydride has become an article of commercial interest, it has been found desirable to substitute a cheaper reagent for the phosphorus compound. In nearly all the commercially practicable processes an anhydrous chloride or oxychloride of sulphur is employed.

Sulphur chlorides. The use of the chlorides of sulphur instead of those of phosphorus has been known for a very long time (Heintz, Jahr. 1856, 560), but these liquids are unpleasant to handle, and their action is not easy to control. The action of sulphur monochloride on the alkali salts of organic acids has been studied by Denham and Woodhouse (Chem. Soc. Trans. 1909, 1235, and 1913, 1861), who used an indifferent solvent to dilute the reagent and control its local action. By treating dry sodium acetate with sulphur monochloride S_2Cl_2, in presence of a neutral solvent, Denham obtained an intermediate compound $(CH_3COO)_2S_2$, which breaks up on heating, according to the equation $2(CH_3COO)_2S_2 = 2(CH_3CO)_2O + SO_2 + 3S$. Denham's reaction, however, does not provide for the maximum technical utilisation of the reagents, since the sulphur dioxide, as an inorganic anhydride, should be capable of taking part in the reaction and should not be allowed to escape unused.

Kessler (Fr. Pat. 315938, 1901), in making use of the action of sulphur chloride on anhydrous sodium acetate, claims that by distilling off the acetic anhydride at a low temperature under reduced pressure, the production of sulphur dioxide is avoided. Whether this is the case or not, it is nevertheless certain that the distillation of the acetic anhydride under reduced pressure constitutes a definite technical advantage when steam-heated vessels are used, and this procedure has remained standard practice in all subsequent methods.

H. Dreyfus (Eng. Pat. 100450, 1916) has clearly set forth the principles which govern the technical manufacture of acetic anhydride by the action of sulphur chloride on dry sodium acetate, in order to avoid the production of sulphur dioxide and of chloroacetic acids by substitution. (*a*) The reagents are used in the proportion of 6 atoms of chlorine to 8 of sodium; (*b*) the reaction is allowed to take place in presence of a diluting agent, in order to avoid any local excess of sulphur chloride and overheating, for which purpose acetic anhydride is most conveniently employed; (*c*) the sulphur chloride is run slowly into the well-cooled mixture of sodium acetate and acetic anhydride and the temperature is not allowed to rise above 15° C. until all the sulphur chloride has been added. For example: a mixture of 720 kilos of dry pulverised sodium acetate and 600 kilos of acetic anhydride is cooled below 0° C., and 306 kilos of sulphur dichloride is gradually introduced, the temperature being maintained at about 0° and the mixture continually stirred. Stirring is continued for some time after all the sulphur dichloride has been added and the anhydride is subsequently distilled off, preferably *in vacuo*. The equations representing this reaction for sulphur monochloride and dichloride respectively may be written:

$$8CH_3COONa + 3S_2Cl_2 = 4(CH_3CO)_2O + 6NaCl + Na_2SO_4 + 5S$$

$$8CH_3COONa + 3SCl_2 = 4(CH_3CO)_2O + 6NaCl + Na_2SO_4 + 2S$$

Thus there is a loss of sulphur which is obviously minimised by employing a sulphur chloride as rich as possible in chlorine. This waste of sulphur may be avoided altogether according to the process of the Akt. Ges. für Anilinfab. (Ger. Pat. 273101; J. Soc. Chem. Ind. 1914, 667) by passing chlorine gas into a mixture of sodium acetate and sulphur chloride at a temperature not exceeding 20° C., thus:

$$8CH_3COONa + SCl_2 + 2Cl_2 = 4(CH_3CO)_2O + 6NaCl + Na_2SO_4$$

The above is a variant of Goldschmidt's process (Eng. Pat. 25433, 1908), in which the whole of the sulphur chloride is generated *in situ* by the action of 6 atoms of chlorine on 1 atom of sulphur at a low temperature in presence of 8-9 mols. of sodium acetate. The sulphur may be replaced by a metallic compound containing sulphur, *e.g.* ferrous sulphide (1st addition to Fr. Pat. 408035), and, according to a later addition to the same patent (Dec. 29, 1910), the intense cooling is not necessary and the reaction may be conducted at temperatures up to 40°-50° C. A similar process is patented by de Jahn (Eng. Pat. 5039, 1910), in which several oxidisable compounds of sulphur may be used, but it is obvious that these must be anhydrous.

Oxychlorides of Sulphur.—Thionyl chloride reacts with dry sodium acetate giving acetic anhydride and sulphur dioxide (G. Wyss, Bull. Soc. Ind. Mul. 1902, 198). Denham and Woodhouse (Chem. Soc. Trans. 1913, 103, 1861) have also studied this reaction, which, however, is not of industrial interest. Sulphuryl chloride, on the other hand, either as such or in the nascent state, is of considerable importance, since it is easily prepared and can be utilised to full advantage according to the equation

$$4CH_3COONa + SO_2Cl_2 = 2(CH_3CO)_2O + 2NaCl + Na_2SO_4$$

The Farbenfab. vorm. F. Bayer und Co. (Eng. Pat. 21560, 1900) treat dry sodium acetate with a mixture of gaseous chlorine and sulphur dioxide at about 20° C. in a closed vessel; to avoid chlorination it is important that the sulphur dioxide be always present in slight excess. According to Farbw. vorm. Meister, Lucius and Bruning (Ger. Pat. 210805, 1907), sulphur dioxide forms a solid addition product with sodium acetate, which is readily decomposed by chlorine with the production of acetyl chloride or acetic anhydride, according to the proportions of sodium acetate used; the reaction may be controlled by mixing the solid addition compound with an anhydrous inorganic salt or with sand. The Badische Co. prepare liquid sulphuryl chloride by mixing the two liquefied gases in a special vessel in presence of a catalyst such as camphor or glacial acetic acid (Eng. Pat. 24255, 1902). Glacial acetic acid and acetic anhydride, being excellent solvents for sulphur dioxide gas, are capable of acting as catalysers for its combination with chlorine gas, and the reaction proceeds quite smoothly without the formation of chloroacetic acids provided the temperature be kept within moderate limits and local excess of chlorine be avoided. Thus in the process of the Akt. Ges. für Anilin fabr., according to Ger. Pat 226218, 1909, sulphuryl chloride is prepared by passing a mixture of sulphur dioxide and chlorine in equivalent proportions into acetic anhydride and separating the product by fractional distillation; the yield is nearly quantitative. It is, however, by no means necessary to isolate the sulphuryl chloride as such, and the same company, according to Eng. Pat. 23924, 1910, employ acetic anhydride both as an absorbing agent for the gases and as a diluting agent for the subsequent reaction with sodium acetate. For instance, 256 parts of sulphur dioxide and 284 parts of chlorine by weight are absorbed in 100 of acetic anhydride and this solution is mixed, while cooling, with 312 parts of sodium acetate; the mixture is stirred and when the reaction is complete, the anhydride is distilled off.

The above summary of methods based on the use of chloro and oxychloro compounds of sulphur covers the majority of the industrial processes successfully practised at the present time. They may all be classed together in one group, in that they may be conceived to yield acetyl chloride as an intermediate product, and their mechanism depends on the intervention of the chlorine ion. To another group belong processes based on the decomposition of sodium acetate with a strong mineral anhydride, such as sulphuric anhydride. Before passing to this second group certain methods of the first group must be mentioned, depending on the use of sulphuric anhydride in conjunction with chlorine as a possible intermediary.

Chlorosulphonic acid SO_3HCl can react with sodium acetate to produce acetyl chloride or acetic anhydride, but only under disadvantageous conditions owing to the presence of the hydracid which liberates acetic acid. The Badische Co. (Eng. Pat. 24255, 1902) proposed to avoid this difficulty by the use of sodium chlorosulphonate, obtained by the action of chlorosulphonic acid on sodium chloride: 150 parts of sodium chlorosulphonate are heated with 170 parts of sodium acetate at 70° C., and the anhydride produced is distilled off. The equation may be written

$$NaSO_3Cl+2CH_3COONa$$
$$=(CH_3CO)_2O+NaCl+Na_2SO_4$$

If half the quantity of sodium acetate be used, acetyl chloride is produced. A similar process in a simplified form has been devised by H. Dreyfus (Eng. Pat. 17920, 1915), who uses a compound formed by the direct absorption of sulphuric anhydride by sodium chloride. In these reactions, the sodium chloride most probably does not serve merely as a vehicle for the absorption of the sulphuric anhydride, but may be assumed to play a part in the reaction through the intermediate formation of pyrosulphuryl chloride $ClSO_2{\cdot}O{\cdot}SO_2Cl$, thus:

$$3NaSO_3Cl=S_2O_5Cl_2+Na_2SO_4+NaCl$$
$$S_2O_5Cl_2+6CH_3COONa$$
$$=3(CH_3CO)_2O+2Na_2SO_4+2NaCl$$

Pyrosulphuryl chloride is formed together with carbonyl chloride by the action of sulphuric anhydride on carbon tetrachloride. Both products are capable of reacting with sodium acetate to produce acetic anhydride, and Beatty (Eng. Pat. 18823, 1912) has proposed to utilise this reaction, but the process hardly appears suitable for commercial application.

Methods of the second group depending on the direct action of inorganic anhydrides without the intervention of chlorine have been far less widely developed, because secondary reactions which destroy the acetic anhydride very readily occur. A method for the direct application of sulphuric anhydride was patented by the Fabriek van Chem. Prod. of Schiedam, Holland (Eng. Pats. 12130 and 12042, 1913), and further described by Van Peski (Chem. Soc. Abst. 1914, i. 653), in which use is made of an addition compound of glacial acetic acid with sulphuric anhydride and its reaction with sodium acetate. The method is attended by certain technical drawbacks, the operations have to be carried out at a very low temperature, and it is impossible to prepare acetic anhydride of high strength owing to the use of acetic acid as a vehicle. According to a process patented by H. Dreyfus (Eng. Pat. 17920, 1915) sulphuric anhydride is absorbed by sodium sulphate to form a solid addition compound which appears to be different from ordinary sodium pyrosulphate: 800 kilos of sulphuric anhydride are added with constant stirring to 1000 kilos of powdered anhydrous sodium sulphate, and the product, when thoroughly cooled, is added to 1640 kilos of sodium acetate suspended in 1600 kilos of acetic anhydride, the mixture being constantly stirred and cooled with water. The reaction is completed by heating at 60°-70° C.

The above account sufficiently summarises the principal processes which are of industrial importance. There are several others of potential interest and some only of academic importance. An excellent review of the subject is contained in a paper by Hewitt and Lumsden (J. Soc. Chem. Ind. 1916, 210). Among the proposed dehydrating agents of minor importance may be mentioned: Silicon tetrafluoride, which may be regenerated by heating the residue with sand and sulphuric acid (Sommer, Fr. Pat. 354742, 1905); Nitric anhydride (Muller, Fr. Pat. 468963, 1914); *p*-Toluenesulphochloride, a by-product of the manufacture of saccharin (von Heyden, Ger. Pat. 123052, 1901).

Recent research has been directed to the synthetic preparation of acetic anhydride from acetylene and acetaldehyde, for instance, according to Fr. Pats. 420346 and 442738, by the action of chlorine or chlorous anhydride. An interesting method is based on the hydration of acetylene to aldehyde in presence of a mercuric salt at the expense of the dehydration of acetic acid (Boiteau, Fr. Pats. 474828 and 475853), with production of ethylidene diacetate, which yields acetic anhydride and acetaldehyde on distillation (Eng. Pats. 23190, 1914; 110906, 1917; and 112765, 1917).

The chemical engineering of the manufacture of acetic anhydride presents no unusual problems. Ample cooling power must be provided to take up the considerable amount of heat produced during the mixing of the reagents. Powerful and effective stirring gear is necessary both in the mixing and the distilling plants to deal with the masses of semi-solid and finally solid materials which result from the reaction. Access of moist air is the principal source of loss, since 1 part of water will destroy 5·7 parts of anhydride.

Crude acetic anhydride is purified and freed from mineral acids and sulphur compounds by redistillation under reduced pressure in presence of sodium acetate and a metallic oxide, *e.g.* copper oxide, which yields an insoluble sulphide. Commercially pure acetic anhydride contains 80-95 p.c. of anhydride, the remainder being acetic acid. A richer product for laboratory purposes may be prepared by fractional distillation.

Physical Constants.—The properties of pure acetic anhydride have been studied by Orton and Jones (Chem. Soc. Trans. 1912, 101, 1720). The pure compound boils at 139·5° C. at 760 mm. pressure, and has sp.gr. 1·0876 at 15°/4° C., and 1·0820 at 20°/4° C. The commercial anhydride containing a little acetic acid boils at about 138° C. The specific heat is 0·434, and the latent heat of vaporisation at 137° is 66·1 Cals. per kilo (Berthelot). The heat of hydration per grm.-mol to form 2 mols. of acetic acid (liquid) is 13·1 Cals. The refractive index for the ray D at 20° C. is 1·39038, and for the ray Hγ is 1·39927 (Landolt).

Chemical Properties.—Acetic anhydride is not immediately hydrolysed on shaking with cold water, and at low temperatures anhydride and water or aqueous acetic acid may remain in contact with each other for a considerable time. At 20° C. and over the hydrolysis proceeds rapidly, and the temperature rises very considerably. The hydration is accelerated by a trace of sulphuric acid. According to Orton and Jones (*l.c.*), 100 grams of pure acetic anhydride dissolve about 2·7 grams of water at 15° C., but the solvent power is considerably increased by the presence of small quantities of acetic acid. Lumière and Barbier (Bl. 1906, 35, 625) have studied the stability of solutions of acetic anhydride in water and alcohol at 15° and 0° C.; 100 parts of cold water dissolve 12 of acetic anhydride on shaking.

When mixed with concentrated sulphuric acid at 0° C. acetic anhydride forms an addition compound, acetylsulphuric acid, which is a viscous syrupy liquid; if the temperature is allowed to rise this changes to the isomeric sulphoacetic acid $HSO_3CH_2{\cdot}COOH$, and brown condensation products are also formed (Stillich, Ber. 1905, 1241). With concentrated nitric acid at a low temperature, acetic anhydride gives a compound $C_4H_9NO_7$, which is described as diacetylorthonitric acid (Pictet and Genequand, Ber. 1902, 2526), and with nitric anhydride it gives acetyl nitrate $C_2H_3O_2NO_2$ (Pictet and Khotinsky, Compt. rend. 1907, 144, 210). These substances react generally with organic hydroxyl compounds as nitrating agents, more rarely as acetylating agents. Acetic anhydride dissolves boric anhydride slowly, boric acid rapidly, on heating, giving a mixed boric acetic anhydride $B(OOC{\cdot}CH_3)_3$, m.p. 121° C. (Pictet and Geleznoff, Ber. 1903, 2219). This substance may be used for the preparation of neutral boric esters by warming with alcohols and phenols. With absolute formic acid at a temperature not exceeding 50° C., acetic anhydride combines to give formyl acetic anhydride which distils with decomposition at 105°–120° C. This compound generally yields formic esters with alcohols and formyl derivatives with amines (Béhal, Bl. 1900, 24, 745; Eng. Pat. 12157, 1899).

Acetic anhydride is employed for the manufacture of cellulose acetate, acetylsalicylic acid (aspirin), and diacetylmorphine (heroin), also in the dyestuffs and pharmaceutical industries; it is largely employed in the laboratory for the quantitative estimation of hydroxyl groups and for the preparation of acetyl derivatives of bases. With aldehyde groups it reacts, forming the diacetates of ortholdehydes

$$R{\cdot}CHO \rightarrow R{\cdot}C(OH)_2 \rightarrow R{\cdot}C(OOC{\cdot}CH_3)_2$$

which are not very stable.

Analysis.—Commercial acetic anhydride should be substantially free from sulphur and phosphorus compounds, chlorides and chloroacetic acids. Copper from the distillation plant and higher homologues, such as propionic and butyric acids, may be objectionable for pharmaceutical or analytical purposes; these may be removed by careful fractionation. The valuation of purified acetic anhydride is performed by simple titration of the total acidity as acetic acid and calculation of the excess of acidity in terms of acetic anhydride. About 5 grams of the sample is accurately weighed in a small weighing tube which is then dropped into 100 c.c. of N/1-sodium hydroxide. When the anhydride has completely disappeared, the excess of alkali is titrated back with N/10-acid in presence of phenolphthalein. If p is the weight of sample taken, and q its acidity as acetic acid, the weight of anhydride present is $5{\cdot}6641\ (q-p)$. The success of this method depends entirely on the accuracy of the measuring vessels and the standardisation of the solutions. An error of 0·1 c.c. of N/1-soda involves an error of 0·7 p.c. in the anhydride result, and the greatest care must be exercised in the calibration of the burettes; it is necessary also to apply a correction for the change in volume of the normal solution at temperatures different from that at which it was standardised. The method of Menschutkin and Vasilieff is based on the formation of acetanilide from aniline at a moderate temperature; it does not give satisfactory results in its original form. For a *résumé* of the various methods and an improved modification of the aniline method, *see* Radcliffe and Medofski, J. Soc. Chem. Ind. 1917, 628. There is no simple and accurate method for the estimation of higher homologues in presence of large proportions of acetic acid; besides the standard analytical text-books, the following references may be consulted: Muspratt, J. Soc. Chem. Ind. 1900, 204; Langheld and Zeileis, Ber. 1913, 1171; Crowell, J. Amer. Chem. Soc. 1918, 413.

J. F. B.

ACETINS. The acetins are the acetyl derivatives of glycerol, or glycerol acetates. Five of these are theoretically possible, two mono-, two di-, and one tri- derivative, according to the number and position of the hydroxyl groups attacked by the acetic acid. Only three of these compounds have been prepared so far, one in each class, and the positions which the acetyl groups take up in the mono- and di- derivatives does not appear to be experimentally proved, though they are probably terminal. Commercial acetin is a mixture of all three compounds with other products.

The following method for the preparation of mono-, di-, and tri-acetin has been described by A. C. Geitel (J. pr. Chem. 1897, [ii.] 55, 41):—

200 grams of dry glycerol are heated with 500 grams of glacial acetic acid for 8 hours, and the acetic acid and water distilled off under reduced pressure. A further quantity of 150 grams acid is then added, and the heating continued for 16 hours. *Triacetin* is isolated from the product by diluting with water and extracting with ether, and is a colourless liquid, dissolving in water to the extent of about 7 p.c. at 15°. It has a sp.gr. 1·1605 at 15° and distils without decomposition at 172°–172·50/40 mm. *Diacetin* is obtained from

the remaining solution by fractionating (after concentration) under a pressure of 40 mm., when it comes over between 175°–176°. It is a soluble colourless liquid with sp.gr. 1·1769 at 15°. In order to isolate the monoacetin formed in the reaction the aqueous solution after removal of the triacetin is extracted for 8 hours with ether at 34°–35° in an extracting apparatus for liquids; the later extracts are collected separately, diluted with an equal volume of water, and, after being extracted with hot benzene, are concentrated. The monacetin thus formed is a thick syrup of sp.gr. 1·2212 at 15°. By prolonging the ether extraction still further *monacetyldiglycerol* $C_3H_5(OH)_2{\cdot}O{\cdot}C_3H_5(OAc){\cdot}OH$ may be obtained; it is a colourless liquid of sp.gr. 1·2323 at 15°. *Diacetyldiglycide* may also be separated from the monacetin by fractionation, and *triacetyldiglycerol* is also formed.

Commercial Acetin ('*Acetine*') is prepared by heating in an oil-bath a mixture of 60 parts of glycerol and 82 parts of glacial acetic acid for 12–15 hours at 120°, and gradually raising the temperature to 160° to expel the excess of acetic acid. The product is a thick liquid smelling of acetic acid and varying in colour from light yellow to dark brown, according to the purity of the glycerol used.

The value of the product depends upon the extent to which combination has taken place, and this is determined by observing the specific gravity and estimating the free and combined acetic acid. The density varies between 1·1608 and 1·1896, being lowest when the free acetic acid is present in largest amount. The free and combined acetic acid are determined as follows: 50 grams of 'acetin' are diluted with water to 500 c.c. The free acid in 50 c.c. of this solution is determined by titration with normal caustic soda, using phenolphthaleïn as indicator. 15 c.c. of normal caustic soda are added to 10 c.c. of the acetin solution, and the combined acetic acid liberated by hydrolysis by boiling for five minutes. The excess of caustic soda remaining is a measure of the total acid present; and the amount of combined acid is found by subtracting from the amount of caustic soda used up in the hydrolysis the quantity accounted for by the free acid. The following table (Kopp and Grandmougin, Bull. Soc. Ind. Mulhouse, 1894, 112) shows the results of typical analyses:—

No	Density	Acid free	Acid combined	Remarks
		p.c.	p.c.	
1	1·1774	9·2	46·0	A medium quality sample
2	1·1896	6·98	55·7	A good sample
3	1·1608	23·0	43·5	Poor sample.

Acetin is used as a solvent for basic colouring matters, such as Induline and Perkin's violet. They are dissolved by being heated together for about two hours, cooling, and filtering through a silk filter. Acetin is to be preferred to ethyl and methyl tartaric acids as a solvent, as acetic acid is less injurious to the fibres than tartaric acid.

Halogen derivatives of the Acetins.

αγ-dibromo-β-acetylglycerol $(CH_2Br)_2CH{\cdot}OAc$ is obtained by the prolonged action of hydrogen bromide on triacetin, or by heating the mixture to 100° in sealed tubes; it boils at 130°–135° (40 mm.) and has sp.gr. 1·5880 at 15°. It has an agreeable aromatic odour, is slightly soluble in water, and readily soluble in alcohol and ether. It yields *iso*propyl alcohol on reduction.

α-bromo-βγ-diacetylglycerol $CH_2Br{\cdot}CH(OAc){\cdot}CH_2{\cdot}OAc$ is produced by the prolonged action of hydrogen bromide dissolved in acetic acid on triacetin at 0° in the dark. It boils at 150°–155° (40 mm.), and has sp.gr. 1·2905 at 15°. It yields *iso*propylene glycol on reduction.

αγ-dichloro-β-acetylglycerol $(CH_2Cl)_2CH{\cdot}OAc$, prepared similarly to the bromine compound, boils at 115°–120° (40 mm.), and has sp.gr. 1·1618 at 15°.

α-chloro-βγ-diacetylglycerol $CH_2Cl{\cdot}CH(OAc)CH_2{\cdot}OAc$ boils at 145°–150° (40 mm.), and has sp.gr. 1·1307 at 15°.

αβ-dichloromonoacetin $CH_2Cl{\cdot}CHCl{\cdot}CH_2{\cdot}OAc$ is prepared by the action of acetic anhydride on chlorinated allyl alcohol, and has sp.gr. 1·1677 at 15°, but in all other respects is identical with the αγ-dichloro- compound.

α-iododiacetin $CH_2I{\cdot}CH(OAc){\cdot}CH_2{\cdot}OAc$ is obtained by the action of sodium iodide on the corresponding chloro- compound. It is an unstable oil having a sp.gr. 1.4584 at 15°.

J. A. P

ACETNAPHTHALIDE DISULPHONIC ACID

v. NAPHTHALENE.

ACETOACETIC ACID $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$ is a thick acid liquid miscible with water in all proportions. It is prepared from its ethyl ester by leaving 4¼ parts of ester in contact with 2·1 parts of potash and 80 parts of water for 24 hours and acidifying with sulphuric acid. It is extracted from the solution with ether.

It is very unstable and readily decomposes below 100° into acetone and carbon dioxide. It yields a violet colouration with ferric chloride and forms ill-characterised amorphous salts, $Ba\bar{A}_2,2H_2O$ and $Cu\bar{A}_2,2H_2O$, when treated with the corresponding carbonate.

Acetoacetic acid appears in the urine of diabetic patients, and indicates defective oxidation. Its detection and estimation have been the subject of much controversy and investigation. Arnold (Chem. Zentr. 1899, ii. 146) makes use of a colour reaction with acetophenone, which will show 1 part in 10,000, but is affected to some extent by the presence of acetone. Riegler (Chem. Soc. Abstr. 1903, ii. 112) employs the colour produced by the addition of sulphuric and iodic acids, which he states to be unaffected by the presence of sugars, leucine, tyrosine, or acetone. Bondi (Chem. Zentr. 1906, i. 707) recommends the use of a solution of iodine and the detection of acetoacetic acid by the characteristic smell of the iodacetone produced; but Lindemann (*ibid.* 717) says that this smell is not characteristic of acetoacetic acid. Mayer adds the urine to a very dilute solution of ferric chloride in brine, when, in the presence of acetoacetic acid, a claret-red ring is formed. When the red colour is only just visible, the liquid may be assumed to contain 0·01 p.c. of the acid. A blank test performed after boiling the acid for five minutes should give no colour (Chem. Zentr. 1906, i. 406).

Messinger's process as modified by Huppert (Analyse des Harns, 1898) estimates the total amount of acetone and acetoacetic acid present with fair accuracy, and the acetone may be estimated separately with considerable exactitude by the method of Folin (J. Biol. Chem. 1907, 3, 177), in which it is aspirated out of the liquid into iodine and potash, and the resulting iodoform weighed.

Methyl acetoacetate $CH_3\cdot CO\cdot CH_2\cdot CO_2Me$ is prepared by heating together methyl acetate and sodium under a reflux condenser and subsequently distilling in a stream of carbon dioxide. It is a colourless liquid, easily miscible with water, which boils at 169°–170° and has a sp.gr. 1·0917 at 4°; 1·0809 at 15°; and 1·0724 at 25°. It is decomposed on boiling with water into carbon dioxide, acetone, and methyl alcohol. With ferric chloride it yields a deep red colouration.

Ethyl acetoacetate (acetoacetic ester) $CH_3\cdot CO\cdot CH_2\cdot CO_2Et$ and $CH_3\cdot C(OH):CH\cdot CO_2Et$, was discovered by Geuther in 1863, and independently by Frankland and Duppa in 1865. It is a colourless, slightly syrupy liquid, with a pleasant odour. It boils at 180·6°–181·2°/754 mm. (Brühl); 180°–180·3°/754·5 mm. (Schiff); 71°/12·5 mm. and 100·2°/80 mm. (Kahlbaum). It has a specific gravity 1·0465 0°/4° (Schiff); 1·0282 20°/4° (Schaum). The density gradually changes on keeping (*v. infra*).

Ethyl acetoacetate is prepared by the action of sodium on ethyl acetate. The following details of the method are given by Conrad (Annalen, 186, 214): 100 grams of sodium are added to 1000 grams of pure ethyl acetate, and after the reaction has moderated considerably, the whole is heated on a water-bath under a reflux condenser for 2–2½ hours until all the sodium has disappeared. To the warm mass 550 grams of 50 p.c. acetic acid are added, and after cooling 500 c.c. of water. The whole is well shaken, and the upper layer separated, washed with a little water, and fractionated. The fractions 100°–130°, 130°–165°, 165°–175°, 175°–185°, 185°–200° are collected separately and refractionated twice. The yield is 175 grams of product boiling at 175°–185°, and from the fraction boiling below 100°, 350–400 grams of ethyl acetate may be recovered after removing the alcohol by salting out. Details of a method of preparation on the large scale are given by Cobenzl in Chem. Zeit. 1914, 38, 665.

Ethyl acetoacetate is neutral to litmus, but forms salts with sodium, copper, and other metals by replacement of hydrogen. Only one atom of hydrogen can be replaced by sodium, but if the sodium in the resulting compound is replaced by an alkyl radicle a second hydrogen atom may then be replaced. Ferric chloride produces a violet colouration. With sodium bisulphite a crystalline addition product $C_6H_{10}O_3$, $NaHSO_3$ is formed. On heating for a long time, or leading the vapour through a hot tube, acetone, alcohol, dehydracetic acid, and methane are formed. Sodium amalgam reduces it to *β-hydroxy butyric* acid $CH_3\cdot CH(OH)\cdot CH_2\cdot CO_2H$. It condenses with hydroxylamine, but does not form an oxime, as internal condensation takes place, resulting in the production of *methyl isooxazolone* $CH_3\cdot C\cdot CH_2\cdot CO$ which is converted by
$\ddot{N}$——$\dot{O}$
alkalis into salts of β-oximinobutyric acid.

Applications in Synthesis.—By means of ethyl acetoacetate fatty acids, ketones, and many ring compounds may be prepared.

Fatty acids may be obtained by dissolving sodium (1 atom) in absolute alcohol, adding ethyl acetoacetate (1 mol.) followed by an alkyl halogen compound (1 mol.). The resulting alkyl derivative is treated with strong alkalis, when the molecule is hydrolysed with formation of acetic acid and the desired alkyl acetic acid.

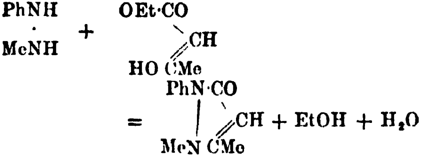
$$CH_3\cdot CO\cdot CH_2\cdot CO_2H \rightarrow CH_3\cdot C(ONa):CH\cdot CO_2Et \rightarrow CH_3\cdot CO\cdot CHR\cdot CO_2Et \rightarrow CH_3\cdot CO_2H + RCH_2\cdot CO_2H$$

If the hydrolysis is brought about by *dilute acids* instead of concentrated alkalis, the molecule is differently divided, producing ketones.

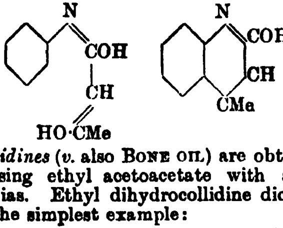
$$CH_3\cdot CO\cdot CHR\cdot CO_2Et \rightarrow CH_3CO\cdot CH_2R + EtOH + CO_2.$$

Dialkyl acetic acids and ketones may be produced by introducing a second alkyl radicle into the molecule by a similar process after the first has entered, but the two cannot be introduced together in one operation.

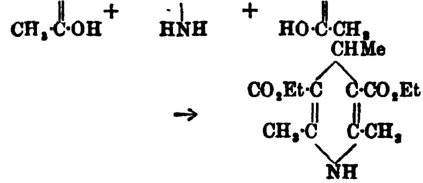
Pyrazolones, of which the most important industrially is *antipyrine*, are produced by the condensation of ethyl acetoacetate with hydrazines. Antipyrin (1-*phenyl* 2:3-*dimethyl*-5-*pyrazolone*) is prepared from symmetrical methyl phenylhydrazine and ethyl acetoacetate (*v.* also PYRAZOLE and ANTIPYRINE).



Quinolines may be prepared by first making the anilide of ethyl acetoacetate by heating with aniline at 110°, and afterwards heating this product with concentrated hydrochloric acid. $CH_3\cdot CO\cdot CH_2\cdot CO\cdot NHPh$ changes into $CH_3\cdot C(OH):CH\cdot C(OH):NPh$, and readily condenses to 1 *hydroxy*-4-*methylquinoline*



Pyridines (*v.* also BONE OIL) are obtained by condensing ethyl acetoacetate with aldehyde ammonias. Ethyl dihydrocollidine dicarboxylate is the simplest example:



Pyrones.—Dehydracetic acid, α-methyl βacetylpyrone, is produced on heating ethyl acetoacetate for a considerable time.

Constitution.—The constitution of ethyl acetoacetate and its sodium derivatives was for many years a subject of discussion by Frankland and Duppa, Geuther, Claisen, Laar, Wislicenus, Brühl, Perkin, and others. The general opinion is that ethyl acetoacetate consists of a mixture of the two forms, ketonic $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$, and enolic $CH_3{\cdot}C(OH):CH{\cdot}CO_2Et$. The freshly prepared substance is practically a pure ketone, but on keeping it changes partially into the enolic form, and when equilibrium is reached about 10 p.c. of the latter is present at ordinary temperatures. The rate of change has been studied by observing the change of viscosity. *See* Dunstan and Mussel, Chem. Soc. Trans. 1911, 99, 566. The sodium compound is a derivative of the enolic form.

Alkyl derivatives of ethyl acetoacetate.

1 *Mono-substituted alkyl derivatives.*

Ethyl methylacetoacetate $CH_3{\cdot}CO{\cdot}CHMe{\cdot}CO_2Et$ boils at 186·8°, and has sp.gr. 1·009 at 6°. Prepared from methyl iodide and sodium acetoacetate (Geuther, J. 1865, 303)

Ethyl ethylacetoacetate $CH_3{\cdot}CO{\cdot}CHEt{\cdot}CO_2Et$ boils at 195°–196°, and has sp.gr. 0·9834 at 16°. It is readily decomposed by baryta or alcoholic potash into alcohol, carbon dioxide and methyl propyl ketone; and by dry sodium ethoxide into acetic and butyric esters (Miller, Annalen, 200, 281; Wedel, Annalen, 210, 100, Frankland and Duppa, Annalen, 138, 215; Wislicenus, Annalen, 186, 187)

Ethyl propylacetoacetate $CH_3{\cdot}CO{\cdot}CHPr^{a}{\cdot}CO_2Et$ boils at 208°–209°, and has sp.gr. 0·981 a 0°/4°. It is prepared by adding to a solution of 27 grams of sodium in 270 grams absolute alcohol, 152·7 grams ethyl acetoacetate, followed gradually by 206 grams propyl iodide.

Ethyl isopropylacetoacetate $CH_3{\cdot}CO{\cdot}CHPr\beta{\cdot}CO_2Et$ boils at 201°/758·4 mm., and has sp.gr 0·9805 at 0°.

Ethyl isobutylacetoacetate $CH_3{\cdot}CO{\cdot}CH(CH_2{\cdot}CHMe_2){\cdot}CO_2Et$ boils at 217°–218°, and has sp.gr. 0·951 at 17·5° (Rohn, Annalen, 190, 306; Minter, Ber. 1874, 501).

Ethyl isoamylacetoacetate $CH_3{\cdot}CO{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CHMe_2)CO_2Et$ boils at 227°–228° (Peters, Ber. 1887, 3322).

Ethyl amylacetoacetate $CH_3{\cdot}CO{\cdot}CH(C_5H_{11})CO_2Et$ boils at 242°–244° (Ponzio and Prandi, Gazz. chem. ital. 28, ii. 280).

Ethyl heptylacetoacetate boils at 271°–273°, and has sp.gr. 0·9324 at 17·7°.

Ethyl octylacetoacetate boils at 280°–282°, and has sp.gr. 0·9354 at 18°·5/17·5°.

2. *Di-substituted alkyl derivatives.*

Ethyl dimethylacetoacetate $CH_3{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et$ boils at 184°, and has sp.gr. 0·9913 at 16°.

Ethyl methylethylacetoacetate $CH_3{\cdot}CO{\cdot}CMeEt{\cdot}CO_2Et$ boils at 198°, and has sp.gr. 0·947 at 22°/17°·5.

Ethyl methylpropylacetoacetate $CH_3{\cdot}CO{\cdot}CMePrCO_2Et$ boils at 214°, and has sp.gr. 0·9575 at 17°/4°.

Ethyl diethylacetoacetate $CH_3{\cdot}CO{\cdot}CEt_2{\cdot}CO_2Et$ boils at 218°, and has sp.gr. 0·9738 at 20°.

Ethyl dipropylacetoacetate $CH_3{\cdot}CO{\cdot}CPr_2{\cdot}CO_2Et$ boils at 236°, and has sp.gr. 0·9585 at 0°/4°.

Ethyl diisobutylacetoacetate boils at 250°–253°, and has sp.gr. 0·947 at 10°.

Ethyl diheptylacetoacetate boils at 332°, and has sp.gr. 0·891 at 17·5°/17·5°.

Ethyl dioctylacetoacetate boils at 264° /90 mm., 340°–342° /760 mm.

ACETOFORM. Trade name for a combination of hexamethylenetetramine and aluminium aceto citrate.

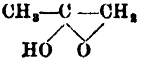
ACETOL (*methyl-ketol, acetyl carbinol,* or *propanolon*) CH_3COCH_2OH is the simplest ketone alcohol. It is obtained by saponification of the acetyl carbinol acetate or formate produced on condensing chloro-acetone with potassium acetate or formate (Henry, Ber. 1872, 5, 966; W. H. Perkin, Trans. Chem. Soc. 1891, 59, 786; Nef, Annalen, 1904, 335, 248). For the purpose of saponification in this case boiling with methyl alcohol containing 1–2 p.c. hydrochloric acid is employed. It is also formed in the biochemical oxidation of propylene glycol by means of the sorbose bacterium or by *mycoderma aceti*, in the pyrochemical decomposition of glycerol (Nef, *l.c.*), and by heating α-bromopropionic aldehyde with a methyl alcoholic solution of potassium or sodium formate for 10–15 hours (Nef, *ibid.* 265). In this latter preparation the metal halide is filtered off and the acetol fractionated twice under diminished pressure, when it is obtained perfectly pure.

Acetol boils at 54° (18 mm.), and with slight decomposition at 147° under atmospheric pressure. It possesses a faint, characteristic smell, and is miscible with water. It readily forms more complex condensation products, especially in the presence of traces of halogen compounds; but this may be avoided by diluting it with its own volume of methyl alcohol. When passed through a tube heated to 450° it decomposes into acetaldehyde and *meta*formaldehyde, together with a small quantity of their decomposition products, namely, crotonaldehyde, carbon monoxide, hydrogen, &c.

On oxidation with mercuric oxide, silver oxide, or chromic acid in the presence of sulphuric acid it yields formic and acetic acids; but with copper oxide in alkaline solution it yields lactic acid:

$$CH_3COCH_2OH \rightarrow CH_3CO\,CHO \xrightarrow{+H_2O} CH_3{\cdot}CHOH{\cdot}COOH$$

On reduction with sodium amalgam in aqueous solution, acetone, *iso*propyl alcohol, and propylene glycol are produced; a reaction which suggests that in aqueous solution acetol has changed into the tautomeric form:



The behaviour of acetol and its esters to the Grignard reagent shows that they exist in the carbonyl form, for with magnesium ethyl iodide, amylene glycol $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CH_2OH\end{matrix}$ is obtained, which could not be the case with the ethylene oxide type of structure. In contact with solid caustic alkali, acetol is converted into dark red tarry matters, with simultaneous development of great heat.

Acetol-oxime is obtained by the oxidation of 2-methyl-2-hydroxyaminopropane di-ol-1·3 $(HONH)(CH_3)C(CH_2OH)_2$, with mercuric oxid-

(Pilotz and Ruff, Ber. 1897, 30, 1656, 3161). It crystallises in prisms, melts at 71° C., and is easily soluble in water.

Acetol semicarbazone

$$CH_3{\cdot}C(:N{\cdot}NH{\cdot}CONH_2){\cdot}CH_2OH$$

serves as the best means of identifying acetol. It melts at 195°–200° C., is very stable, and is only very slightly soluble in ether, benzene, and chloroform. The *phenylhydrazone* melts at 106° C.; the *osazone* at 153°–154° C.

The name 'Acetol' is also given to a product obtained as an ester of salicylic acid by condensing sodium salicylate with monochloracetone $OH{\cdot}C_6H_4{\cdot}COO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$. Forms needles from solution in alcohol, m.p. 71°; sparingly soluble in warm water (Fritsch, E. P. 3961, 1893; J. Soc. Chem. Ind. 1894, 274).

ACETOMETER. A hydrometer graduated to indicate the strength of commercial acetic acid according to its density.

ACETOMORPHINE. Syn. for diacetylmorphine. Used to check spasmodic coughing, and in lowering reflex irritability, *v.* OPIUM and OPIUM ALKALOIDS.

ACETONE C_3H_6O or $CH_3{\cdot}CO{\cdot}CH_3$. *Dimethyl ketone.* A product of the destructive distillation of acetates; obtained by Liebig from lead acetate (Annalen, 1, 225) and further examined by Dumas (Ann. Chim. Phys. [2] 49, 208), who first determined its composition. Acetone is also produced in the dry distillation of wood (Völckel, Annalen, 80, 310; J. Soc. Chem. Ind. 16, 667, 722; 27, 798); of citric acid (Robiquet, B. J. 18, 502); of sugar, starch, and gums with lime (Frémy, Annalen, 15, 279; J. Soc. Chem. Ind. 21, 541, 1006). Large quantities of acetone are now produced by the destructive distillation of the giant kelp of the Pacific Coast; the quantity of cut kelp averaged above 24,000 tons a month in 1917. By oxidation of proteid substances with iron salts (Blumenthal and Neuberg, Chem. Zentr. 1901, i. 788; Ingler, Beitr. Chem. Phys. Path. 1902, i. 583), and by heating citric acid with potassium permanganate (Péan de St. Gilles, J. 1858, 585; Sabbatani, Atti Acad. Sci. Torino, 1900, 35, 678); and by the oxidation of *iso*valeric acid (Crossley and Le Sueur, Chem. Soc. Trans. 1899, 165). Acetone is also produced by the Fernbach process, in which starch from maize or other grain is fermented by a special ferment which resolves the carbohydrate into a mixture of butyl alcohol and acetone.

Preparation.—1. Acetone can be obtained by distilling a mixture of 1 part of caustic lime and 2 parts of crystallised lead acetate (Zeise, Annalen, 33, 32); but is usually prepared by the dry distillation of barium acetate at a moderate heat. Calcium acetate can also be employed, but the temperature required is greater, and the product is contaminated with impurities, such as *dumasin*, an isomeride of mesityl oxide; but according to Becker (J. Soc. Chem. Ind. 26, 279) a lower temperature is required if the calcium salts are made quite neutral and the formation of free lime is prevented by the introduction of a stream of dry carbon dioxide. Bamberger (Ber. 1910, 43, 3517) considers that the formation of acetone consists first in the formation of lime and acetic anhydride, and that the latter is decomposed into acetone and carbon dioxide. It has been shown (Freudenheim, J. Physical Chem. 1918, 22, 184) that when acetone is heated with lime at temperatures ranging up to 630°, a species of 'cracking' occurs, which results in the formation of methane, ethylene, hydrogen, carbon monoxide, and carbon dioxide. As the temperature is raised to the upper limit mentioned, the amount of methane increases rapidly, whilst that of hydrogen is diminished. The explanation put forward is that acetone undergeos (*a*) a high temperature dissociation; and (*b*) conversion into keten, which thereafter decomposes:

$$\begin{aligned} CH_3{\cdot}CO{\cdot}CH_3 &\rightarrow CH_4+CO+C+H_2 \\ CH_3{\cdot}CO{\cdot}CH_3 &\rightarrow CH_4+CH_2:CO \\ 2CH_2:CO &\rightarrow 2CO+C_2H_4 \end{aligned}$$

Magnesium or strontium acetates can also be used. Industrially, acetone can be prepared by passing the vapour of acetic acid into air-tight vessels heated to 500°, containing some porous substances saturated with lime or baryta (J. Soc. Chem. Ind. 18, 128, 824; Bauschlicker, D. R. P. 81914); also by passing a continuous current of pyroligneous acid over a heated acetate capable of forming acetone (J. Soc. Chem. Ind. 25, 634; 26, 1002; 27, 277). An improved method is also described by Wenghoffer (D. R. P. 144328; compare also J. Soc. Chem. Ind. 14, 987; 20, 1130; 22, 297).

According to Squibb (J. Soc. Chem. Ind. 1896, 231; J. Amer. Chem. Soc.), pure acetone for use in the preparation of smokeless powders can be obtained by subjecting acetates mixed with an excess of calcium hydroxide to destructive distillation and to the action of superheated steam.

2. From wood spirit acetone can be separated by distilling over calcium chloride. The product obtained by these methods can readily be purified by converting the acetone into its crystalline compound with acid sodium (or potassium) sulphite, crystallising this, and subsequently distilling with aqueous sodium carbonate; the distillate is then treated with concentrated calcium chloride solution and the ethereal layer rectified over solid chloride. According to Conroy (J. Soc. Chem. Ind. 19, 206), it should be purified by distillation over sulphuric acid (Dott, J. Soc. Chem. Ind. 27, 272), whilst Arnoult (*ibid.* 27, 679) recommends treatment with oxidising agents.

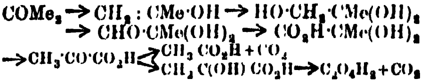
According to Shipsey and Werner (Chem. Soc. Trans. 1913, 103, 1255), sodium iodide forms a crystalline compound with acetone $NaI,3C_3H_6O$, which easily gives off all the acetone on gentle warming. The formation of this compound can be used for the preparation of pure acetone from the commercial material. It may be readily prepared by dissolving anhydrous sodium iodide to the point of saturation in the hot acetone, and allowing the solution to cool to the ordinary temperature; if the liquid is cooled to about −8° by means of ice and salt, the yield of crystals is largely increased.

Acetone has been prepared synthetically from zinc methyl and acetyl chloride (Freund, Annalen, 118, 11). It occurs in the urine, blood, and brain of calcium diabetic patients.

Properties.—Acetone is a limpid, mobile liquid, having an agreeable odour and a peppermint-like taste. It is very inflammable and burns with a white smokeless flame, b.p. 56·3° (Regnault); sp.gr. 0·8144 at 0°, 0·79945 at 13·9° (Kopp, Annalen, 64, 214); b.p. 56·1°–56·2° (corr.), and sp.gr. 0·8137 at 0°/4° (Shipsey and Werner); 56·22° (corr.) and sp.gr. 0·81[illegible]58 0°/4° (Thorpe and Rodger); sp.gr. 0·81378 at 0°/4°, 0·79705 at 15°/4°, 0·77986 at 30°/4° (Saposchnikoff, J. Russ. Phys. Chem. Soc. 28, 229); m.p. −94·9° (Ladenburg and Krugel, Ber. 32, 1821; Formenti, L'Orosi, 1900, 23, 223). Acetone is miscible in all proportions with water, alcohol, ether, and many ethereal salts; it can be separated from its aqueous solution by the addition of calcium chloride, and dissolves many fats and resins. It is also an excellent solvent for acetylene and tannins (Trimble and Peacock, Pharm. J. 53, 317). Acetone is used in perfumery and pharmacy; in the manufacture of smokeless powders; of cordite and of celluloid articles (Marshal, J. Soc. Chem. Ind. 23, 24, 645), also in the preparation of iodoform (Teeple, J. Amer. Chem. Soc. 26, 170; Abbott, J. Phys. Chem. 7, 83); of chloroform (Squibb, J. Amer. Chem. Soc. 1896, 231; Orndorff and Jessel, Amer. Chem. J. 10, 363; Dolt, *l.c.* 271); and in the presence of sodium sulphite it can be used as a good substitute for alkali in photographic developers (Lumière and Segewetz, Bull. Soc. chim. 15, [3] 1164; Mon. Sci. 1903, 257, 568; Eichengrun, Zeitsch. angew. Chem. 1902, 1114). When its vapour is passed through a red-hot copper tube, a very small proportion of tarry products containing naphthalene is obtained together with a large volume of gas having the composition: carbon monoxide, 39·23 p.c.; methane, 37·58 p.c.; hydrogen, 17·54 p.c.; and ethylene, 5·65 p.c. (Barbier and Roux, Compt. rend. 102, 1559). Dehydrating agents readily act on acetone and convert it into condensation products; thus, caustic lime converts acetone into mesityl oxide $C_6H_{10}O$ and phorone $C_9H_{14}O$ when the action is allowed to continue for a week (Fittig, Annalen, 110, 32), and, together with smaller proportions of other products, these two compounds are also formed when it is saturated with hydrogen chloride and allowed to stand for 8 to 14 days (Baeyer, Annalen, 140, 297): with zinc chloride terpene condensation products are formed (Raikow, Ber. 30, 905). Distillation with concentrated sulphuric acid converts acetone into mesitylene, mesityl oxide, phorone and *iso*durene and other substances (Orndorff and Young, Amer. Chem. J. 15, 249). A similar result is obtained when it is heated with boron fluoride. The action of nitric acid and nitric oxide on acetone has been studied by Newbury and Orndoff (Amer. Chem. J. 12, 517), Behrend and Schmitz (Annalen, 277, 310), Behrend and Tryller (Annalen, 283, 209), Apetz and Hell (Ber. 27, 933), Traube (Annalen, 300, 81), McIntosh (Amer. Chem. Soc. 27, 1013); of hydrogen peroxide by Baeyer and Villiger (Ber. 32, 3625; 33, 174, 858), Pastureau (Compt. rend. 140, 1591), Wolffenstein (Ber. 28, 2265); of thionyl chloride by Loth and Michaels (Ber. 27, 2540); and of hypophosphorous acid by Marie (Compt. rend. 133, 219).

Sodium in the presence of water reduces acetone to *iso*propyl alcohol and pinacone (Fittig, Annalen, 110, 25; 114, 54; Städeler, Annalen, 111, 277; Friedel, Annalen, 124, 329), but when the materials are quite dry and air is excluded, sodium acetonate is formed (Freer, Amer. Chem. J. 12, 355; 13, 308; 15, 582; Taylor, Chem. Soc. Trans. 1906, 1258; Bacon and Freer, Philippine J. Sci. 1907, 2, 67). Red-hot magnesium acts on acetone, yielding hydrogen and allylene, whilst magnesium amalgam forms magnesium acetonate which is rapidly decomposed by water, yielding pinacone hydrate (Keiser, Amer. Chem. J. 18, 328; Conturier and Meunier, Compt. rend. 140, 721). Anhydrous acetone, in presence of metallic calcium, is slowly converted at the ordinary temperature into mesityl oxide (Raikow, Chem. Zeit. 1913, 37, 1455). Chlorine, bromine, and iodine in the presence of alkalis convert acetone into chloroform, bromoform, and iodoform respectively.

Reactions.—When quite pure acetone should remain perfectly colourless on exposure to light, and should not be attacked by potassium permanganate in the cold; in the presence of alkali, however, and on warming, carbonic and oxalic acids are formed (Cochenhausen, J. pr. Chem. 166, 451; Conroy, J. Soc. Chem. Ind. 19, 206; Fournier, Bull. Soc. chim. 1908, 3, 259). According to Witzemann (J. Amer. Chem. Soc. 1917, 39, 2657), the oxidation process involves preliminary enolisation of the acetone, followed by the formation of pyruvic acid.



$$\mathrm{COMe_2 \rightarrow CH_2:CMe{\cdot}OH \rightarrow HO{\cdot}CH_2{\cdot}CMe(OH)_2 \rightarrow CHO{\cdot}CMe(OH)_2 \rightarrow CO_2H{\cdot}CMe(OH)_2 \rightarrow CH_3{\cdot}CO{\cdot}CO_2H} \begin{cases} \mathrm{CH_3\,CO_2H + CO_2} \\ \mathrm{CH_2\,C(OH)\,CO_2H \rightarrow C_2O_4H_2 + CO_2} \end{cases}$$

Acetone, when treated with aqueous potash and iodine, yields iodoform (Lieben). Gunning (Zeitsch. anal. Chem. 24, 147) has modified this reaction to render it available when alcohol is present by employing ammonia and a solution of iodine in ammonium iodide. Another test proposed by Reynolds (*ibid.* 24, 147) is based on the fact that mercuric oxide is soluble in acetone in the presence of potassium hydroxide; the suspected liquid is mixed with a solution of mercuric chloride rendered strongly alkaline with alcoholic potash, and after shaking the mixture is filtered and the filtrate tested for mercury by means of ammonium sulphide or stannous chloride. Denigès (Compt. rend. 126, 1868; 127, 963; Bull. Soc. chim. 13, [3] 543; 19, [3] 754) recommends the use of the additive compound formed by acetone with mercury sulphate, for detecting acetone in methyl and ethyl alcohol (Oppenheimer, Ber. 32, 986). Penzoldt (Zeitsch. anal. Chem. 24, 147) adds to the suspected liquid orthonitrobenzaldehyde, which in presence of caustic alkali combines with acetone to form indigo. Another delicate test is to add sodium hydroxide, hydroxylamine and pyridine, then ether and bromine until the solution is yellow, hydrogen peroxide is now added when, if acetone is present, the solution becomes blue (Stock); dimethyl *p*-phenylenediamine produces a red colouration which changes to violet on addition of alkali or acid (Malerba, Zeitsch. anal. Chem. 37, 690). Similar colour reactions are obtained by adding a few drops of sodium nitroprusside to a mixture of acetone and a primary aliphatic amine (Rimini, Chem. Zentr. 1893, 2, 132). Of all these tests Lieben's is perhaps the most sensitive. To detect acetone in urine a strong solution of sodium nitroprusside is added, then the mixture made alkaline with potash, when a red colouration is produced which changes to violet on addition of acetic acid (Legal, J. Pharm. Chim. 1888, 17, 206; Denigès, Bull. Soc. chim. [3] 15, 1058). According to Egeling (Chem. Zentr. 1894, ii. 457), it is best to use ammonia, when a brilliant violet colour is at once produced: this reaction is not given by aldehyde. For other methods of detecting and estimating acetone, compare Arachequesne, Compt. rend. 110, 642; Collischonn, Zeitsch. anal. Chem. 29, 562; Squibb, J. Amer. Chem. Soc. 18, 1068; Kebler, *ibid.* 19, 316; Schwicker, Chem. Zeit. 15, 914; Strache, Monatsh. 13, 299; Klar, J. Soc. Chem. Ind. 15, 299; Hintz, Zeitsch. anal. Chem. 27, 182; Sternberg, Chem Zentr. 1901, i. 270; Keppeler, Zeitsch. angew. Chem. 18, 464; Vaubel and Schleuer, *ibid.* 18, 214; Jolles, Ber. 39, 1306; Auld, J. Soc. Chem. Ind. 25, 100; Heikel, Chem. Zeit. 32, 75.

(For estimating acetone in wood spirit, *see* Arachequesne, *l.c.*; Vignon, Compt. rend. 110, 534; 112, 873; and in urine, *see* Huppert, Zeitsch. anal. Chem. 29, 632; Salkowski, J. Pharm. Chim. 1891, 194; Geelmuyden, Zeitsch. anal. Chem. 35, 503; Willen, Chem. Zentr. 1897, i. 134; Martz, ii. 232; Argenson, Bull. Soc chim. 15, [3] 1055; Studer, Chem. Zentr. 1898, i. 1152; Mallat, J. Pharm. 1897, 6296; Sabbatani, Chem. Zentr. 1899, ii. 22; Riegler, Zeitsch. anal. Chem. 40, 94; Vournasos, Bull. Soc. chim. 31, [3] 137; Graaff, Pharm. Weekblad, 1907, 44, 555; Folin, J. Biol. Chem. 1907, 3, 177; Monimart, J. Pharm. Chem. 1892, 26, 302; Heikel, *l.c.*; Hart, J. Biol. Chem. 1908, 4, 477.)

Derivatives.—Acetone combines directly with a large number of substances yielding well-characterised additive compounds. 1. *Compounds with alkaline sulphites*:—Acetone forms definite crystalline compounds when shaken with concentrated solutions of the acid sulphites (bisulphites) of the alkali metals (Precht, Phot. Centr. 1902, 8, 301; Kerp, Kaiserl. Gesundh. 1904, 21, 40; Rothwood, Monatsh. 26, 1545). The *potassium* salt $C_3H_6O,KHSO_3$, and the *sodium* salt $C_3H_6O,NaHSO_3$, crystallise in nacreous scales (Limpricht, Annalen 93, 238); the *ammonium* salt C_3H_6O,NH_4HSO_3 crystallises in laminæ (Städeler, Annalen, 111, 307). The *barium* salt has formula $2C_3H_6O,Ba(SO_3H)_2,H_2O$ (Fagard, J. Pharm. Chim. 1895, 2, 145). These salts yield acetone when heated with aqueous potash. *Calcium chloride* combines with acetone to form $CaCl_2,2C_3H_6O$ and $CaCl_2,C_3H_6O$ (Bagster, Chem. Soc. Trans. 1917, 111, 494).—2. *Compounds with chloroform* (Willgerodt, Ber. 14, 2451; 15, 2308; Cameron and Holly, Chem. Zentr. 1898, ii. 277; Jocitsch, *ibid.* 1899, i. 606; Willgerodt and Dürr, J. pr. Chem. 148, 283). —3. *Compounds with hydrogen cyanide* (Urech, Annalen, 164, 255):—Acetone yields acetone-cyanhydrol C_4H_7NO, b.p. 120°, when added to anhydrous hydrogen cyanide; and diacetone-cyanhydrol $C_7H_{13}NO_2$, a crystalline substance, when treated with a 25 p.c. solution (aqueous) of hydrogen cyanide (Tiemann and Friedländer, Ber. 14, 1965); with 3·3 p.c. hydrogen cyanide acetone-cyanhydrin is obtained in the dark, but in the light a mixture of products is formed (Silber, Ber. 38, 1671).—4. *Compounds with ammonia*:—Ammonia unites with acetone in the cold with the elimination of the elements of water; the reaction, however, proceeds more quickly if the temperature is raised to 100°, or if dry ammonia gas is passed into boiling acetone. Several bases, diacetonamine $C_6H_{13}NO$, triacetonamine $C_9H_{17}NO$, triacetonediamine $C_9H_{20}N_2O$, and dehydrotriacetonamine $C_9H_{15}N$; the last two in very small quantity only, have been obtained by these methods, the relative proportions in which they are formed varying with the temperature and time employed. These bases and their derivatives have been examined by Heintz (Annalen, 174, 133; 175, 252; 178, 305, 326; 181, 70; 183, 276; 189, 214; 191; 122; 198, 42, 87; 201, 90; 203, 336) and by Sokolow and Latschinow (Ber. 7, 1384), Ruhemann and Carnegie (Chem. Soc. Trans. 1888, 424), Rügheimer (Ber. 21, 3325; 25, 1562), Harries (Annalen, 296, 328), Franchimont and Friedmann (Rec. Trav. Chim. 1907, 223), Gabriel and Colman (Ber. 35, 3805), Kohn and Lindauer (Monatsh. 23, 754), Kohn (Annalen, 351, 13[illegible]; Monatsh. 24, 765, 773; 25, 135, 817, 850; 28, 429, 508, 529, 537, 1040); they yield well-crystallised salts, and can be separated from one another by means of their oxalates. Methylamine also gives corresponding compounds with acetone, but dimethylamine yields dimethyldiacetonamine as the sole product (Göttschmann, Annalen, 197, 27).

Thioacetones have been studied by Baumann and Fromm (Ber. 22, 1035, 2592). Acetone forms compounds with mercuric sulphate (Denigès, *l.c*; Oppenheimer, *l.c.*), with mercuric oxide (Auld and Hantzsch, Ber. 38, 2677; Lasserre, J. Pharm. Chim. 1890, 22, 246), with mercuric cyanide (Marsh and Struthers, Chem. Soc. Trans. 1905, 1878), with mercuric iodide (Gernez, Compt. rend. 137, 255; Marsh and Struthers, Chem. Soc. Proc. 1908, 266), and with mercuric nitrate (Hofmann, Ber. 31, 2212). Metallic derivatives of the type $CH_3{\cdot}CO{\cdot}CH_2K$ are obtained by the electrolysis of acetone solutions of potassium or sodium iodides or of potassium thiocyanate (Levi and Voghera, Gazz. chim. ital. 35, i. 277).

Acetone yields substitution derivatives when acted upon with chlorine or bromine (Bischoff, Ber. 5, 863, 963; 8, 1329). The following derivatives have been obtained:—Monochloracetone (Henry, Ber. 5, 190; Mulder, Ber. 5, 1009; Barbaglia, Ber. 7, 467; Linnemann, Annalen, 134, 171; Koenigs and Wagstaffe, Ber. 26, 554; Wislicenus, Kircheisen and Sattler, *ibid.* 26, 908; Fritsch, *ibid.* 26, 597; Tcherniac, Ber. 25, 2629; Kling, Bull. Soc. chim. [3] 33, 322); unsymmetrical dichloracetone (Fittig, Annalen, 110, 40; Borsche and Fittig, Annalen, 133, 112· Erlenbach, Annalen, 269, 46; Tcherniac, *l.c.*; Fritsch, *l.c.*; McIntosh, Chem. Soc. Trans. 1905, 790); symmetrical dichloracetone (Barbaglia, *l.c.*; Fritsch, *l.c.*); trichloracetone (Bischoff, *l.c.*; Kraemer, Ber. 7, 252; Perrier and Prost, Compt. rend. 140, 146; Hantzsch, Ber. 21, 242); tetrachloracetone (Bischoff, Levy, Witte and Curchod, Annalen, 252, 330, 254, 83; Levy and Jedlicka, Ber. 21, 318); and pentachloracetone (Cloëz, Bull. Soc. chim. [2] 39, 638; Fritsch, Annalen, 279, 310 and *l.c.*; Levy and Jedlicka, *l.c.*). Pentachloroacetone treated with phosphorus pentachloride yields as-heptachloropropane C_3Cl_{10}, a crystalline substance, m.p. 32°; also obtained by the direct addition of chloroform to tetrachloroethylene under the influence of aluminium chloride (Böeseken and Prins, Proc. K. Akad. Wetensch. Amsterdam, 1911, 13, 685). The corresponding bromo-derivatives, with the exception of tribromacetone, are obtained by the direct action of bromine upon acetone (Mulder, J. 1864, 330; McIntosh, *l.c.*; Lapworth, Chem. Soc. Trans. 1904, 33), also by other methods (Hjelt and Siven, Ber. 21, 3288; Norton and Westenhoff, Amer. Chem. J. 10, 213; Hartzsch, *l.c.*). Other halogen derivatives (J. Soc. Chem. Ind. 16, 933; Hantzsch, *l.c.* and Ber. 22, 1238) and the compounds of acetone with the halogen acids (Archibald and McIntosh, Chem. Soc. Trans. 1904, 924) have been described.

Acetone forms a large number of condensation products and derivatives with other organic compounds: Cyanacetones (Hantzsch, Ber. 23, 1472; Tche niac, Ber. 25, 2607, 2621; Kowppa, Ber. 33, 3530). Acetone dioxalic ester obtained by the action of sodium ethylate on a mixture of acetone and oxalic ester is converted when treated with sodium ethoxide to a dienolic substance forming lemon-yellow needles, m.p. 98°, and dyeing wool in alcoholic solution It is the first nitrogen free dye-stuff of the fatty series yet obtained (Willstatter and Pummerer, Ber. 37, 3733). Pseudo*cyclo*citralidene acetone and its homologues have an odour of violets, and are suitable for use in perfumes (J. Soc Chem. Ind. 24, 200).

For acetone dicarboxylic acid and its derivatives, *see* Ormerod, Chem. Soc. Proc. 1906, 205, Denigès, Compt. rend. 128, 680; Lippmann, Ber. 41, 3981; for acetonyl acetone and its derivatives, *see* Knorr, Ber. 22, 168, 2100; Claisen and Ehrhardt, Ber. 22, 1009; Zincke and Kegel, Ber. 23, 230; Claisen, Ber. 25, 3164; the azo- (Bulow and Schlotterbeck, Ber. 35, 2187) and diazo- derivatives of acetonyl acetone, have dyeing properties (Faurel, Compt. rend. 128, 318).

Acetone, with diazobenzene chloride in the presence of alkali, yields a compound $C_{15}H_{14}ON_2$ m.p. 134°–135°, which has dyeing properties (Bamberger and Wulz, Ber. 24, 2793). For other condensation products compare Boessneck, Ber. 21, 1906; Pechmann and Wehsarg, *ibid.* 2989, 2994; Franke and Kohn, Monatsh. 19, 354; 20, 876; Spier, Ber. 28, 2531; Perkin and Thorpe, Chem. Soc. Trans. 1896, 1482; Weidel, Monatsh. 17, 401; Micko, *ibid.* 442; Stobbe Ber. 28, 1122; Cornelson and Kostanecki, Ber. 29, 240; Claisen, *ibid.* 2931; Röhmer, Ber. 31, 281; Pfitzinger, J. pr. Chem. 164, 283; Freer, Amer. Chem. J. 17, 1; Barbier and Bouveault, Compt. rend. 118, 198; Haller and March. Compt. rend. 139, 99; Straus, Ber. 37, 3293 Harries and Ferrari, Ber. 36, 656; Ulpiani and Bernardini, Atti R. Accad. Lincei, 1904, 13, 331; Pechmann and Sidgwick, Ber. 37, 3816; Duntwitz, Monatsh. 27, 773; Knoevenagel, Ber. 39, 3451, 3457; Purdie, Chem. Soc. Trans. 1906, 1200; Richard, Compt. rend. 145, 129. Diacetones and their derivatives have been studied by Combes (Compt. rend. 108. 1252; Behal and Auger, Compt. rend. 109, 970; Claisen and Stylos, Ber. 21, 141); derivatives of triacetone by Weinschenk (Ber. 34, 2185).

ACETONECHLOROFORM, *ααα-trichlor-β-hydroxy-β-methylpropane* (*Chloretone*) $(CH_3)_2 \cdot C(OH) \cdot CCl_3$, prepared by slowly adding powdered potassium hydroxide (3 parts) to a cooled mixture of acetone (5 parts) and chloroform (1 part) (Willgerodt, J. pr. Chem. [2] 37, 361) is a white crystalline compound, b.p. 167°, melting near but above 97°; it has a camphor-like odour, is soluble in hot, sparingly soluble in cold water, and crystallises well from ether, alcohol, acetic acid, acetone, or chloroform; it forms no definite hydrate, but the system acetone-chloroform/water presents a quadruple point for the solid, two solutions and the vapour at 75·2° (Cameron and Holly, J. Phys. Chem. 1898, 2, 322). The *acetate* $(CH_3)_2 \cdot C(OAc) \cdot CCl_3$ boils at 191°. The *benzoate* $(CH_3)_2 \cdot C(OBz).CCl_3$ boils at 282° (Willgerodt and Dürr, J. pr. Chem. [2] 39, 283). Acetonechloroform is reduced by zinc-dust and alcohol, forming dichloro*iso*butylene, *iso*crotylchloride, and *iso*butylene (Jocitsch, J. Russ. Phys Chem. Soc. 1898, 30, 920); and is decomposed by water at 180°, yielding hydrogen chloride and hydroxy*iso*butyric acid (Willgerodt, Ber. 1882, 15, 2305). By the action of benzene in presence of aluminium chloride the chlorine atoms of acetonechloroform are replaced wholly or in part by phenyl residues, and the compounds *diphenylchloromethyl dimethyl carbinol* $CPh_2Cl \cdot CMe_2 \cdot OH$ b.p. 230°; *phenyldichloromethyl dimethyl carbinol* $CPhCl_2 \cdot CMe_2 \cdot OH$ b.p. 217°; and *triphenylmethyl dimethyl carbinol* $CPh_3 \cdot CMe_2 \cdot OH$ b.p. 260°, have been prepared, and similar compounds are obtained using toluene or *p*-xylene (Willgerodt, J. pr. Chem. [2] 37, 361).

Acetonechloroform is a powerful germicide, a satisfactory surgical dressing, and hypnotic for internal use (Aldrich and Houghton, Amer. J. Physiol. 1900, 3, 26); it is used as a specific for sea-sickness (Merck. Ann. Report, 1907, 1), forming the chief ingredient of "Zotos," and a 1 2 p.c. solution is used under the name of *anesin* for producing local anaesthesia (Cohn, Pharm Zentr. H. 40, 33).

ACETONEDICARBOXYLIC ACID *v.* KETONES.

ACETONE OIL is the oily residue remaining after the separation of acetone from the products of the dry distillation of calcium acetate. It can also be prepared by the dry distillation of the lime salts obtained by neutralising fleece washings with milk of lime. About 15 litres of the oil are obtained from a cubic metre of fleece washings of 11°B. It is a slightly-coloured liquid of sp.gr. 0·835, having a penetrating smell and acrid burning taste. It consists mainly of methyl ethyl ketone (A. and P, Buisine, Compt. rend. 126, 351; 128, 561). According to Duchemin (Bull. Soc. chim. [3] 21, 798) acetone oil is of very variable composition, depending upon the nature of the pyrolignate from which it is prepared. A French Commission reported that it was effective as a denaturant of alcohol and it was adopted for this purpose by the Swiss Government in 1895.

For details of mode of manufacture from wool washings, *v.* Buisine (J. Soc. Chim. Ind. 18, 292; 21, 164); P. Baechlin, (Rev. Chim. Ind. 9, 112; 15, 240).

ACETONIC ACID, *v.* HYDROXYBUTYRIC ACID.

ACETOPHENONE. *Phenyl methyl ketone. Hypnone* $C_6H_5{\cdot}CO{\cdot}CH_3$, is obtained by acting with benzoyl chloride on zinc methyl; by distilling a mixture of the calcium salts of benzoic and acetic acids; or by boiling together benzene and acetyl chloride with aluminium chloride. It can be isolated from the fraction of heavy oil of coal tar boiling at 160°–190° by addition of sulphuric acid, distilling the solution in steam and converting the distillate into the *p*-bromophenylhydrazone derivative of acetophenone (Weissgerber, Ber. 36, 754). It is best obtained synthetically by adding small quantities of sublimed ferric chloride (7 parts) to a mixture of benzene (5 parts) and acetyl chloride (7 parts) diluted with carbon disulphide. The mixture is then warmed on the water-bath, dried and fractionated (Nencki and Stoeber, Ber. 30, 1768).

Acetophenone crystallises in large plates, m.p. 20·5°; b.p. 202°. It possesses a persistent odour of oil of bitter almonds and cherry laurel water; is insoluble in water, but dissolves easily in alcohol, ether, chloroform, or benzene. It is readily oxidised by potassium permanganate to phenylglyoxylic acid (Glücksmann, Monatsh. 11, 246). By the action of ammonia on an alcoholic solution of acetophenone, the acetophenone ammonia is formed $CMePh(N : CMePh)_2$, m.p. 115° (Thomae, Arch. Pharm. 244. 643) (*v.* KETONES).

Acetophenone forms a large number of derivatives and condensation products with aldehydes, halogens, acids, mercury salts, &c. By the action of hydrogen in presence of finely divided nickel it may be converted into phenyl methyl carbinol.

Acetophenone was discovered by Dujardin-Beaumetz and Bardet to possess powerful soporific properties (Compt. rend. 101, 960; Karmensky, Liss. Med. Chi. Acad. St. Petersburg, 1888-1889, No. 70). In quantities of 0·05 to 0·15 gram, it induces a quiet sleep, but is said to impart a disagreeable odour to the breath (Pharm. J. 1886, 582).

Aminoacetophenone (Camps, Arch. Pharm. 40, 15), b.p. 250°–252°; 135°/17 mm., has anæsthetic properties, which are not diminished by condensing it with aldehydes containing a phenolic hydroxyl, but are destroyed when it is condensed with benzaldehyde, tolualdehyde, or cinnamaldehyde (Hildebrandt, Chem. Zentr. 1905, ii. 502; Scholz and Huber, Ber. 37, 390; Schäfer, Ber. 39, 2181).

p-Amino acetophenone v. KETONES.

Acetophenonephenetidene, m.p. 88°, an antipyretic substance, can be obtained by heating molecular proportions of acetophenone and *p*-phenetidene *in vacuô*, then distilling *in vacuô* at 210°–212° (Valentiner, J. Chem. Soc. Ind. 15, 50; 17, 602).

β-ACETO-PROPIONIC ACID. *Lævulic acid*

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H.$$

This substance is formed by the action of dilute acids on a number of carbohydrates—*e.g.* levulose, inulin, galactose. It is also a product of oxidation of the terpene alcohols, but is best prepared by heating on the water-bath cane sugar with dilute hydrochloric acid (4 vols. water, 1 vol. conc. acid) until a brown flocculent precipitate is no longer formed. (Compare Tollens, Ber. 17, 668; Wehmer a. Tollens, Annalen, 243, 214.) The filtered liquid is then evaporated on the water-bath extracted several times with ether, and after distilling off the ether the residue is fractionated in a vacuum.

It can be obtained by the hydrolysis of various nucleic acids (Kossel and Neumann, Zeitsch. physiol. Chem. 27, 2215; Inouye, *ibid.* 42, 117; Levene, *ibid.* 43, 119). For other methods of preparation, compare Tiemann and Semmler (Ber. 28, 2129); Verley (Bull. Soc. chim. [3] 17, 190); Erlenmeyer (J. pr. Chem. 179, 382); Blaise (Bull. Soc. chim. [3] 21, 647).

Lævulic acid crystallises in plates which melt at 33°. It boils at 239°, 148°–149°/15 mm. (Michael, J. pr. Chem. 152, 113), and has at 15° a sp.gr. 1·135. It is very soluble in water, alcohol, or ether, and is not attacked by bromine in the cold. Nitric acid converts it into carbon dioxide, acetic acid, succinic and oxalic acids. Iodine and sodium hydroxide form iodoform even in the cold. Hydriodic acid and phosphorus at 200° convert it into normal valeric acid; whereas sodium amalgam forms sodium γ-hydroxyvalerate acid in an alcoholic solution, and normal valeric acid in an acid solution. When added to boiling iodic acid solution diiodoacetoacrylic acid is formed (Angeli and Chiassi, Ber. 25, 2205). When placed over sulphuric acid in a vacuum it decomposes, leaving a residue of dihydroxyvaleric acid (Berthelot and André, Compt. rend. 123, 341).

The mercury salt $Hg(C_5H_7O_3)_2$, which crystallises in silvery plates, breaks up on treatment with sodium hydroxide, forming the two mercurilævulic acids $C_5H_6O_3Hg$ and $C_5H_4O_3Hg_2$. Lævulic acid readily condenses with benzil (Japp and Murray, Chem. Soc. Proc. 1896, 146), and with aldehydes (Meingast, Monatsh. 26, 265). It forms a semi-carbazone, m.p. 187° (Blaise, *l.c.*). The ethyl ester when treated with ethyl magnesium bromide yields a lactone, b.p. 105°–106°/18 mm. (Grignard, Compt. rend. 135, 627). Halogen substitution derivatives of lævulic acid have also been obtained (Wolff, Ber. 26, 2216; Wolff and Rüdel, Annalen, 294, 192; Conrad and Schmidt, Annalen, 285, 203).

The substance is employed on a manufacturing scale as a mordant instead of acetic acid, as it possesses the advantage of not being volatile with steam.

It is also used in the preparation of the antipyretic *antithermin*. Phenylhydrazine is dissolved in dilute acetic acid, and on adding a solution of lævulic acid a yellow precipitate is formed, which is purified by recrystallisation from alcohol (Pharm, J. [3] xvii. 801) (*v.* ANTITHERMIN).

ACETOPURPURINE *v.* AZO- COLOURING MATTERS.

ACETOPYRINE or **ACOPYRINE.** A combination of phenyl-dimethyl pyrazolone (antipyrine) and acetyl salicylic acid.

ACETOSAL or **ACETYSAL.** Syn. for acetyl salicylic acid.

ACETO-*p*-TOLUIDIDE is obtained by the action of acetic acid upon toluidine. Melts at 153° and boils at 307°.

ACETOZONE. Mixture of acetylbenzoyl

peroxide $\begin{matrix}C_6H_5\cdot CO\\CH_3\cdot CO\end{matrix}\!\!>O=O$ and kieselguhr, used as an antiseptic.

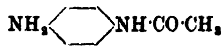
ACETPHENETIDENE *v.* PHENACETIN.

ACETYLCHOLINE *v.* ERGOT, MUSCARINE.

ACETYL-1-NAPHTHYLAMINE-5-SULPHONIC ACID is prepared by boiling a mixture of 5 parts of 1-naphthylamine-5-sulphonic acid, glacial acetic acid, acetic anhydride and sodium acetate under a reflux condenser until a sample cannot be diazotised. The mixture is then heated so long as acetic acid and acetic anhydride distil over.

ACETYL-1 : 4-NAPHTHYLENEDIAMINE-6-SULPHONIC ACID is obtained by adding monoacetyl 1 : 4 naphthylenediamine sulphate to fuming sulphuric acid containing 20 p.c. SO_3, warming to 40°-50° and pouring into ice-cold water. Or a mixture of 1-naphthylamine-6 and 7-sulphonic acids (Cleve's Acids) may be acetylated with glacial acetic acid, distilling off the excess of acetic acid, dissolving the product in sulphuric acid and adding a cooled mixture of nitric and sulphuric acids. The mixture is diluted with cold water and the sodium salts of the nitro-acids precipitated by adding common salt. The mixture of the nitro-acids is reduced by iron filings and acetic acid, made alkaline by sodium carbonate, filtered hot, slightly acidified and the 1 : 4-naphthylenediamine-6-sulphonic acid precipitated. This is acetylated by boiling with a mixture of acetic acid and sodium acetate (Levinstein, Eng. Pat. 12119 (1898); Cassella and Co. D.R.P. 116922). Used in making Diaminogen blues. (Çain, 'Intermediate Products for Dyes.') *Cf.* NAPHTHALENE.

ACETYL-*p*-PHENYLENEDIAMINE (*p*-amino acetanilide)



$NH_2\cdot C_6H_4\cdot NH\cdot CO\cdot CH_3$

is prepared by reducing *p*-nitroacetanilide with iron filings and acetic acid at 60°, rendering the solution alkaline with sodium carbonate and adding common salt and hydrochloric acid when the hydrochloride of acetyl-*p*-phenylene diamine crystallises out (Grandmougin, Rev. prod. chim. 1917, 20, 260). Acetyl-*p*-phenylenediamine melts at 162·5°.

ACETYLENE C_2H_2 is the first member of the series of unsaturated aliphatic hydrocarbons to which it gives its name, and having the general formula : C_nH_{2n-2}. This formula also applies to the dialkylenes the difference being that members of the acetylene series are characterised by the presence of one triple linkage whilst the dialkylenes possess two double linkages :—

$CH\vdots CH$	$CH\vdots C\cdot CH_3$	$CH_3\cdot C\vdots C\cdot CH_3$
Acetylene (C_2H_2).	Propine (C_3H_4) (or Methyl acetylene or Allylene).	Butine (C_4H_6) (Dimethyl acetylene or Crotonylene.)
and	$CH_2\cdot C:CH_2$	$CH_2:CH\cdot CH:CH_2$
	Propadiene (C_3H_4).	Butadiene (C_4H_6).

The dialkylenes will not therefore be considered in this section. (*See* SYNTHETIC RUBBER, ISOPRENE, BUTADIENE.)

Nomenclature.—According to the Geneva system acetylene is to be termed Ethine, the ending -ine being the systematic termination for members of the acetylene series, thus : propine, butine, etc. In practice, however, the original name acetylene is always used as being well established and unlikely to cause confusion. With the exception of allylene C_3H_4, and crotonylene C_4H_6, higher members of the series are usually named as substituted acetylenes, *e.g.* methyl-acetylene, dimethyl-acetylene, isopropyl-acetylene, phenyl-acetylene, &c.

Historical.—Acetylene was first observed by Edmund Davy as a gas produced on treating with water the impure residues obtained in the preparation of potassium (Brit. Assoc. Rep. 1836, p. 62 : Annalen, 23, 144). The first systematic examination of the gas was made by Berthelot (Compt. rend 54, 640 ; Annalen, 123, 212 ; Ann. Chim. Phys [7] 23, 444 ; [8] 6, 182), who examined the composition and properties of acetylene and showed its production in many pyrochemical processes.

Of particular interest to the technical chemist is the discovery by Wöhler, in 1862 (Annalen, 124, 220), that acetylene is produced by treating calcium carbide with water, a discovery that served thirty years later as the starting point for the whole acetylene industry when it was shown by Willson, in 1802, that calcium carbide could be produced on a large scale and in fairly pure condition in the electric furnace. For more than a decade after the introduction of calcium carbide on a commercial scale, the chief interest in the subject lay in the direction of the utilisation of the gas for illuminating purposes, as it was widely believed that the pure white light of acetylene, and its convenience of manufacture in small quantities, would soon cause it to oust coal-gas from the field to a great extent. This expectation has not been fulfilled, though acetylene continues to be of great use for various purposes such as flares, &c. The next stage was the use of the oxy-acetylene flame for the 'autogenous welding' of iron, an industry that to-day utilises a considerable amount of the gas. In the first decade of the present century attempts were made to effect the chemical utilisation of acetylene in various ways, chiefly by the addition of chlorine and the formation of various chlorine derivatives of different boiling-points which are suitable as solvents for many purposes and serve to replace inflammable materials such as benzene, gasoline, and so on, for dry-cleaning, fat-extraction, &c. On these lines much useful work has been done in this country by Tompkins, and by the Clayton Aniline Company, and abroad by the Chemische Fabrik Griesheim-Elektron, and the Consortium für elektrochemische Industrie G.m.b.H. Lastly, since 1910, it has been found possible to produce acetaldehyde direct from acetylene on a technical scale by the use of mercury salts as catalysts, with the result that progress in this field has been remarkably rapid, and the production of such diverse substances as alcohol, acetic acid, acetic anhydride, and acetone from acetylene on a commercial scale is already an accomplished fact which may have vast economic consequences. (*See* ACETALDEHYDE.)

Production.—(1) *By the direct union of carbon and hydrogen* in the electric arc

$$2C+H_2=C_2H_2$$

(Berthelot, Compt. rend. 54, 640 ; Annalen, 123, 212; Ann. Chim. Phys. [7] 23, 444; [8] 6, 182; Bone and Jerdan, Chem. Soc. Trans. 71, 41; 79, 1042; Pring and Hutton, Chem. Soc. Trans. 89, 1600; v. Wartenberg, Zeitsch. angew. Chem. 52, 310.)

(2) *From ethylene dibromide or dichloride* by the action of alcoholic potash, with the intermediate formation of vinyl chloride or bromide:

$$CH_2Br{\cdot}CH_2Br-HBr = CH_2:CHBr$$
$$CH_2:CHBr-HBr = CH:CH$$

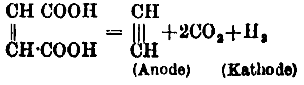
(Sawitsch, Compt. rend. 52, 157; Miasnikow, Annalen, 118, 330; de Wilde, Ber. 7, 352; Sabanejew, Annalen, 178, 109; Zeisel, Annalen, 191, 368; de Forcrand, Compt. rend. 104, 697; Mouneyrat, Bull. Soc. chim. [3] 19, 184; Meunier and Desparment, Compt. rend. 144, 273; Bull. Soc. chim. [4] 1, 342.

(3) *By treating various halogen compounds with metals, e.g.* by treating tetrachlorethane with metallic zinc:

$$CHCl_2{\cdot}CHCl_2+2Zn = CH:CH+2ZnCl_2$$

(Sabanejew, Annalen, 216, 252), or by the action of silver, copper, or zinc dust on iodoform, or by the action of the copper-zinc couple on bromoform (Cazeneuve, Compt. rend. 97, 1871; 113, 1054).

(4) *By electrolysis of unsaturated carboxylic acids*, such as fumaric or maleic acid:



$$\begin{array}{l}CH{\cdot}COOH\\ \|\\ CH{\cdot}COOH\end{array} = \begin{array}{l}CH\\ |||\\ CH\end{array} + 2CO_2 + H_2$$

(Anode) (Kathode)

(Kekulé, Annalen, 131, 85).

(5) *From acetylene mono- or di-carboxylic acids:*

$$C_2(COOH)_2 = C_2H_2+2CO_2$$

(Lossen, Annalen, 272, 140). (*Cf.*, however, Vanzetti and Fasoli, Gazz. chim. ital. 46, i. 49.)

(6) *From propargyl aldehyde* by the action of alkali:

$$CH:C{\cdot}CHO+NaOH = CH:CH+H{\cdot}COONa$$

(Claisen, Ber. 31, 1023).

(7) *By decomposition of various complex organic substances*: *e.g.* brom-cyclo butene (*cf.* Knorr and Matthes, Ber. 32, 740; Willstatter and v. Schmaedel, Ber. 38, 1994; Gabriel, Ber. 38, 2405.)

(8) *From copper acetylide* by the action of aqueous potassium cyanide (Baeyer, Ber. 18, 2273; *cf.* also Zeisel, Annalen, 191, 368; Römer, Annalen, 233, 182; Noyes and Tucker, Amer. Chem. J. 19, 123). This method is stated to yield extremely pure acetylene: if hydrochloric acid be used instead of potassium cyanide, the gas is not so pure and possibly contains traces of vinyl chloride.

(9) *By the action of water on calcium carbide:*

$$CaC_2+H_2O=Ca(OH)_2+C_2H_2$$

Strontium and barium carbides act similarly. (Wöhler, Annalen, 124, 220; Travers, Chem. Soc. Proc. 1893, 15; Maquenne, Compt. rend. 115, 558; Moissan, Bull. Soc. chim. [3] 11, 1007; Lewes, J. Soc. Chem. Ind. 16, 33; Clowes, *ibid.* 209, 319; Wilson, *ibid.* 15, 103; Lüpke, Elektr. Chem. Zeit. 1895, 145; Wyatt, J. Soc. Chem. Ind. 14, 135, 796; 20, 109; Bamberger, Zeitsch. angew. Chem. 1898, 720). This is by far the most convenient and practicable method for the production of acetylene, and is invariably used for the commercial production of the gas.

A convenient laboratory method for the production of acetylene is to cover calcium carbide with absolute alcohol and to add water drop by drop (Matthews, J. Amer. Chem. Soc. 22, 106).

For the technical production of acetylene and its use as an illuminant, *see* ACETYLENE—COMMERCIAL APPLICATIONS.

Details as to the British Patents dealing with the subject will be found in the Patent Office Abridgement Lists, Class 2, (1855–1909) and Class 2 (i) (1910–1915).

Acetylene is produced in the incomplete combustion of various gases such as coal-gas, for instance, when a Bunsen burner 'strikes back.' The view, however, that the accompanying unpleasant odour is due to the acetylene is incorrect. (*Cf.* Meyer and Jacobson, Lehrbuch der organ. Chemie. 2nd edn., I. 1, p. 853, note 2.)

It is also produced by passing methane or natural gas through incandescent carbon (Knapp, U.S. Pat. 1023783).

The chief objection to acetylene produced from calcium carbide is the fact that the various impurities present in the carbide, such as calcium sulphide, phosphide, etc., evolve the corresponding hydrides on treatment with water, so causing the acetylene produced to be contaminated with various small amounts of gases such as ammonia, phosphine, sulphuretted hydrogen, arsine, in addition to other hydrocarbons, carbon monoxide, hydrogen, nitrogen and oxygen.

Phosphine is probably the most serious impurity from the chemical as well as the physiological point of view.

A method of producing odourless acetylene has been patented by S. Ide (Jap. Pat. 30209, 1916), consisting in carbonising calcareous materials which contain phosphorus, sulphur, etc., as impurities, in the electric furnace, spraying with water, whereby the impurities escape in gaseous form, and then using the pure lime so produced for the manufacture of carbide in the usual way; this method would, however, probably be too costly to be of much use, and in practice the crude acetylene can be satisfactorily cleared of all its active impurities by suitable purification such as scrubbing with various liquids—for instance, acidified copper sulphate solution, chromic acid in acetic or sulphuric acid—or with lime, lead or mercury salts, bleaching powder, etc.

(Clowes, J. Soc. Chem. Ind. 16, 209, 319; Lunstroem, Chem. Zeit. 23, 180; Bergé and Reychler, Bull. Soc. chim. [3] 17, 218; Gottig, Ber. 32, 1879; Rossel and Landrisset, Zeitsch. angew. Chem. 1901, 77; Caro, J. Soc. Chem. Ind. 22, 17; 23, 15; Ullmann and Goldberg, Chem, Zentr. 1899, ii. 19; Pfeifer, J. f. Gasbel, 44, 548; Jaubert, J. Soc. Chem. Ind. 24, 116; Willgerodt, Ber. 28, 2107; Hoffmeister, Zeitsch. anorg. Chem. 48, 137; Matthews, J. Amer. Chem. Soc. 22, 106; Ditz, D.R.P. 162324; Lunge and Cedercreutz, Zeitsch. angew. Chem. 1897, 651; J. Soc. Chem. Ind. 16, 37; 24, 1294; 27, 798; Wolff, J. f. Gasbel. 1898, 41, 683. Full details regarding British Patents dealing with the purification of acetylene may be found in the Patent Office 'Fifty Year Subject Index, 1860-1910,' Class 2 (i).)

Properties.—Acetylene is a colourless gas having, in a pure state, a pleasant ethereal odour (Grehaut, Berthelot and Moissan, Compt. rend. 121, 564), which is, however, usually disguised by the presence of fœtid smelling impurities (Zeisel, Annalen, 191, 368; Römer, Annalen, 233, 182; Noyes and Ticker, Amer. Chem. Jour. 19, 123). It solidifies in liquid air to a crystalline mass which can be burnt like a candle (Ladenburg, Ber. 31, 1968). At the ordinary pressure its melting-point (−81°) is higher than its boiling point (−82·4°) (Ladenburg and Krügel, Ber. 32, 1821; 33, 638, Hunter, Chem. Zentr. 1906, ii. 485). McIntosh and Maass give the melting point as −81·5°, sublimation point −83·6°, and boiling point −88·5° (J. Phys. Chem. 11, 306; J. Amer. Chem. Soc. 36, 737); −84·0° Burrell and Robertson. Its critical temperature is 37·05° (Ansdell, Proc. Roy. Soc. 29, 209; Heilbronn, Zeitsch. physical. Chem. 7, 604) or 36·5° (McIntosh, *ibid.*); its critical pressure 67–68 atm. (Leduc, Ann. Chim. Phys. [7] 15, 87) or 61·6 atm. (McIntosh, *ibid.*) and its critical volume 83 c.c. (McIntosh, *ibid.*). Cardosa and Baume give the critical temperature as 35·5° and the critical pressure as 61·5 atm. (Compt rend. 151, 141). For other physical constants of solid and liquid acetylene, see McIntosh, *ibid.*

Liquid acetylene is a mobile fluid of sp.gr. 0·451 at 0° C. (Cailletet, Compt. rend. 85, 851; Ansdell, Jahresbericht d. Chem. 1879, 68) or 0·73 at −75° (McIntosh, *ibid.*). It has a high electrical resistance which is not appreciably altered by the addition of alcohol, ether, halogen hydride, etc. (McIntosh, *ibid.*).

Acetylene is readily soluble in many organic solvents; thus at 18° chloroform and benzene absorb about four times their volume, acetic acid and alcohol about six times their volume (Berthelot, Ann. Chim. Phys. [4] 9, 425; Garelli and Falciola, Atti d. Reale Accad. dei Lincei [5] 13, i. 110). It is extremely soluble in acetone (Claude and Hess, Compt. rend. 124, 626; Claude, Compt. rend. 128, 303) which absorbs twenty-five times its volume of the gas at 15° C. and 760 mm., and under 12 atm takes up 300 volumes, whilst at −80° it absorbs more than 2000 volumes acetylene, which would seem to point to acetone and liquid acetylene being miscible in all proportions. According to McIntosh (*supra*), crystalline compounds are formed. This property of acetone is of great technical importance in the storage of dissolved acetylene for illuminating purposes. (*See* ACETYLENE—COMMERCIAL APPLICATIONS.) (Berthelot and Vieille, Compt. rend. 123, 523; 124, 966, 988, 996, 1000; Wolff, Zeitsch. angew. Chem. 1898, 919; Caro, J. Soc. Chem. Ind. 25, 1138.)

In water the gas is sparingly soluble, about 1 p.c. by volume at 12° and 755 mm. being taken up; it forms a hydrate $C_2H_2+6H_2O$ (Villard, Compt. rend. 120, 1262). The solubility is lowered by the addition of salt (Claude and Hess, *v.s.*). Acetaldehyde has also been suggested as a solvent or diluent for acetylene as it dissolves half its weight of the gas (James and Watson, U.S. Pat. 928867; James, J. Ind. Eng. Chem. 5, 115), the solvent power of organic solvents appearing in general to be associated with the presence of a carbonyl group and low molecular weight.

Acetylene is an endothermic compound, being formed from its elements with an absorption of approximately 50 Cals. As a consequence both the gas and the liquid are highly explosive, particularly under pressure, for which reason solvents are used for storage, as noted above. (*Cf.* Maquenne, Compt. rend. 121, 424; Berthelot and Vieille, Compt. rend. 123, 523; 124, 988, 996, 1000; 128, 777; Ann. Chim. Phys. 11, 5; 17, 303; Claude, Compt. rend. 128, 303; Berthelot and Le Chatelier, Compt. rend. 129, 427; Ann. Chim. Phys. 20, 15; Mixter, Chem. Zentr. 1900, 1, 504; ii. 1007; Chem. Ind. 20, 53).

The molecular heat of combustion is 312·9 Calories at constant pressure. (For other thermal properties see also Berthelot, Compt, rend. 82, 24; Ann. Chim. Phys. [5] 9, 165; 13, 14; 23, 180; Berthelot and Matignon, Ann. Chim. Phys. [6] 30, 556; Maneuvrier and Fournier, Compt. rend. 124, 183; Mixter, Chem. Zentr. 1901, ii. 1250; 1905, ii. 98; 1906, ii. 414; Thomsen, Zeitsch. physical. Chem. 52, 346).

Acetylene when pure has no action on metals (Clowes, J. Soc. Chem. Ind. 16, 109; Moissan, Compt. rend. 124, 566), but ordinary acetylene readily attacks copper owing to the presence of impurities which facilitate the formation of explosive copper acetylide (Scheiber and Reckleben, Chem. Zeit. 39, 42; 40, 325). Nickel and tin in particular are little attacked by acetylene, and it is suggested by Scheiber and Reckleben that metals exposed to the action of acetylene should be coated with one of these metals. It is non-poisonous in small quantities, but may produce asphyxiation when more than 40 p.c. is present (Clowes, *l.c.*; Korda, Mon. Sci. 45, 409; Mosso and Ottolenghi, Ann. di. Chim. e. di. Farmacol. 25, 163; Vitali, Chem. Zentr. 1898, ii. 586; Moissan, *l.c.*; Gréhaut, Compt. rend, 121, 564; Berthelot, Compt. rend. 121, 566; Brociner, *ibid.* 121, 773; J. Soc. Chem. Ind. 16, 319; Rosemann, Chem. Zentr. 1895, ii. 998; Bettinck, Pharm. Weekblad, 54, 413). It has also distinct action on plants (Grafe and Richter, Botan. Zentr. 119, 423).

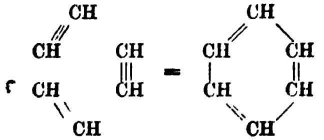
Acetylene explodes very violently when mixed with oxygen or air in any proportion from 3-82 p.c., but the explosiveness is reduced by admixture with inert gases (Meyer, Ber. 27, 2764; Le Chatelier, Compt. rend. 121, 1144; Gréhaut, Compt. rend. 122, 832; Berthelot and Vielle, *ibid.* 123, 523; Bone and Cain, Chem. Soc. Proc. 1896, 176; Clowes, J. Soc. Chem. Ind. 15, 90, 418, 701, 891; Bundt, Ber. 31, 5; Clowes, Chem. Soc. Proc. 1896, 413; Berthelot and Vielle, Compt. rend. 128, 177; *cf.* also Delépine, 8th Intern. Congr. Appl. Chem. 4, 25, and J. Gasbel, 57, 65).

It has been proposed to use acetylene as an explosive for bringing down material, *e.g.*, coal in large pieces (Sprengstoffe, Waffen und Munition, 9, 41).

With ozone acetylene is violently decomposed (Otto, Ann. Chim. Phys. 13, 166).

Pyrogenetic Condensations.—On heating acetylene it undergoes various condensations which are of great importance, particularly in connection with the theory of gas manufacture.

Berthelot found (Jahresbericht f. Chem. 1866, 516; Ann. Chim. Phys. [4] 9, 446, 469) that on leaving acetylene for a time in a glass tube heated to its softening point, a mixture of solid and liquid hydrocarbons was formed in which benzene predominated :—



(*cf.* also Haber, Ber. 29, 2691) It therefore appears probable that the formation and polymerisation of acetylene play an important part in the production of aromatic hydrocarbons in the manufacture of coal-gas (V. B. Lewes, Proc. Roy. Soc. 55, 90; 57, 394). R. Meyer and his co-workers have found that on passing acetylene through a tube suitably heated in an electric furnace large quantities of tarry products are produced, and as a result of collecting several kilos of tar they were able to isolate and identify some 23 products identical with those occurring in ordinary gas-tar, over 20 p.c. being benzene (R. Meyer and others, Ber. 45, 1609; 46, 3183; 47, 2765; 50, 422; 51, 1571) Bone and Coward, however, take a different view, holding that the main gaseous product at high temperatures must be methane which may dissociate into free radicals, CH; and CH_2: which condense together in various ways as the gases cool down (Chem. Soc. Trans. 93–4, 1197).

For a very complete discussion of the subject see 'The Pyrogenesis of Hydrocarbons,' Part I., E. Lawson Lomax; Part II., A. E. Dunstan and F. B. Thole, Journ Ind. and Eng. Chem. 1917, 879, 888; Journ. Inst. Petroleum Technologists, 3, 36–120. A comprehensive bibliography is given in the articles.

At temperatures above 800° or so, acetylene is completely decomposed into hydrogen and free carbon, possibly with the intermediate formation of methane :

$$2C_2H_2=3C+CH_4=4C+2H_2$$

(*Cf.* Bone and Coward, *l.c.*)

This method has been patented for the production of pure hydrogen, the finely divided carbon so produced having a considerable commercial value as *acetylene black* (*cf.* J. Soc. Chem. Ind. 178, 711; 18, 284; 20, 955; Dépierre, *ibid.* 20, 890; Frank, Zeitsch. angew. Chem. 1905, 1733).

Thus Morehead (U.S. Pat. 986480) claims a process for dissociating acetylene by passing it suddenly into a chamber heated to at least dull redness. Before the war the Carbonium Co., at Friedrichshaven, had a factory in which compressed acetylene was decomposed by means of electricity into acetylene black and hydrogen, the latter being used for the Zeppelin airships; it is improbable, however, that the process can compete with other methods for the production of cheap hydrogen such as the Messerschmidt process or the Frank-Caro method (*v.* HYDROGEN).

Pictet (Eng. Pat. 24256, 1910) claims the production of hydrogen and carbon from acetylene by allowing it to flow into an externally heated chamber to be there heated until dissociation takes place, that part of the conduit through which the constituents pass being cooled so as to absorb the excessive heat produced by the reaction.

Acetylene burns with a very smoky but brilliantly white flame which can be modified by mixing carbon dioxide with the gas, the intensity varying with the concentration of the latter (Alvisi, Ann. chim. applicata, 5, 118). When submitted to the action of an electric discharge at ordinary pressure various condensation products are formed (*cf.* Berthelot, Bull. Soc. chim. [3] 4, 480; Jackson and Laurie, Chem. Soc. Proc. 1906, 155; Losanitsch, Monatsh. 29, 753; Javitschitsch, *ibid*, 29, 1; 29, 5; Coehn, Zeit. f. Elektr. 7, 681; Billitzer, Monatsh, 23, 199; Schutzenberger, Compt. rend. 110, 889).

Owing to its unsaturated nature acetylene readily enters into reactions to form addition products. It adds on hydrogen to form ethylene and ethane :

$$C_2H_2+H_2=C_2H_4$$
$$C_2H_2+2H_2=C_2H_6$$

This is most effectively performed with the aid of nascent hydrogen in the presence of a catalyst. Thus Lane (Eng. Pat. 10724, 1911) claims the synthesis of ethylene from acetylene and hydrogen by passing them over a heated catalyst contained in a series of tubes. (*Cf.* also Atterbury, Eng. Pat. 2961, 1898; Wideen, Eng. Pat. 9340, 1903; Bouchard-Praceiq, Eng. Pat. 6075, 1905.) Karo (D. R. P. 253160) claims the production of ethylene from acetylene and hydrogen using as a catalyst a mixture of at least one metal of the palladium or platinum group with at least one metal of the following series: iron, nickel, cobalt, copper, silver, magnesium, zinc, cadmium, or aluminium.

B. E. Eldred and G. Mersereau (U.S. Pat. 1308777) also put forward somewhat similar claims, the catalyst used being nickel or palladium on a carrier of coke, asbestos, pumice, etc.; to prevent the action becoming too energetic the gas mixture is diluted with ⅓ to ½ its volume of carbon dioxide or ethane.

According to Paal and his co-workers acetylene is readily reduced to ethylene and ethane by hydrogen in the presence of colloidal platinum or palladium; in presence of palladium practically pure ethylene can be obtained, the reduction being step-wise; in presence of platinum 35–40 p.c. of ethane is produced simultaneously (Ber. 43, 2684, 2692; 48, 275, 1195, 1202; 46, 128; Chem. Zeit. 36, 60. *Cf.* also de Wilde, 7, 353; Sabatier and Senderens, Compt. rend. 130, 1559, 1628, 1761; 131, 40, 187, 267; Bull. Soc. chim. [3] 25, 678).

W. Traube and W. Passarge (Ber. 49, 1692) describe the reduction of acetylene directly to ethylene by means of an aqueous solution of chromous chloride; the same result is obtained if powdered zinc, diluted hydrochloric acid and a small quantity of chromous chloride be used. No ethane appears to be produced under such conditions. The reaction may be carried out under pressure (D. R. P. 287585; U.S. Pat. 1179051).

When passed over various metallic catalysts such as finely reduced nickel, copper, cobalt or iron, a mixture of acetylene and hydrogen may yield various liquid hydrocarbons as well as ethylene and ethane: in particular copper yields a greenish hydrocarbon, 'Cuprene' (*q.v.*) $(C_7H_6)_n$, as also does nickel (Sabatier and Senderens, Compt. rend. 128, 1173; 130, 250, 1559, 1628; 131, 187; Moreau, *ibid.* 122, 7240; Alexander, Ber. 32, 2381; Erdmann and Köthner, Zeitsch. angew. Chem. 18, 49; Gooch and Baldwin, *ibid.* 22, 235).

By passing acetylene over the kathode of alkaline lye undergoing electrolysis ethylene and ethane are formed (Billitzer, Monatsh. 23, 199).

With fuming sulphuric acid acetylene gives a sulphonic acid, the potassium salt of which, $(C_2H_2)_3\cdot(SO_4KH)_4$, yields phenol on fusion with potash and distilling the product (Berthelot, Compt. rend. 127, 908; 128, 333; Ann. Chim. Phys. [7] 17, 289; Schroeter, Ber. 31, 2189; Muthmann, Ber. 31, 1880). If 50 p.c. fuming sulphuric acid be used the chief product is *acetaldehyde disulphonic acid*:

$$CH{\vdots}CH+2H_2SO_4=(SO_3H)_2\cdot CH\cdot CHO+H_2O$$

(Schroeter, Muthmann, *l.c.*). Atterbury (Eng. Pat. 1208, 1898) claims the production of vinyl alcohol by passing acetylene into hot strong sulphuric acid.

When led into fused alkali at 220° acetylene is completely absorbed and hydrogen is liberated. The reaction product on treatment with water gives alkali acetate. A 60 p.c. yield is claimed but the process hardly seems of commercial value (Feuchter, Chem. Zeit. 38, 273). It reacts with hypochlorous acid to give *dichlor-acetaldehyde*,

$$\begin{aligned}C_2H_2+HClO &= CHCl_2\cdot CH(OH)_2\\ &= CHCl_2\cdot CHO+H_2O\end{aligned}$$

(Wittorf. Chem. Zentr. 1900, ii. 29).

With nitric acid nitroform and various complex nitrogenated substances are produced including an explosive substance $C_4H_2O_3N_4$ m.p. 78° (Tustoni and Mascarelli, Gazz. chim. ital. 31, i. 461; Mascarelli, *ibid.* 33, ii. 319).

According to K. J. P. Orton (Eng. Pat. 125000) a good yield of tetranitromethane may be obtained from acetylene and nitric acid by passing the gas into 90 p.c. to 97 p.c. acid, preferably in presence of a small quantity of mercury, at about 40° C., adding sulphuric acid and then distilling off the tetranitromethane formed.

Water forms an addition product at low temperatures and under pressure, of the formula $C_2H_2\cdot 6H_2O$ (Villard, Compt. rend. 120, 1262; Ann. Chim. Phys. [7] 10, 396; 11, 360; Berthelot, Compt. rend. 128, 336; Ann. Chim. Phys. [7] 17, 297; Forcrand and Thomas, Compt. rend. 125, 109). It does not, however, combine with water directly to form acetaldehyde except in the presence of catalysts such as salts of cadmium, magnesium, zinc, and especially mercury (Kutscherow, Ber. 14, 1540; 17, 13; 42, 2759; Erdmann and Köthner, Zeitsch. angew. Chem. 18, 48):

$$CH{\vdots}CH+HOH = CH_2:CH(OH) \rightarrow CH_3\cdot CHO$$

This property has of recent years given rise to many important developments, as acetaldehyde can be readily converted into most diverse substances such as alcohol, acetic acid, acetone, butadiene and so synthetic rubber, etc. (For further details see ALDEHYDE.)

When mixed with gases such as ammonia, sulphuretted hydrogen, &c., and passed through heated tubes, various condensation products are formed identical with those occurring in coal-tar, such as pyridine, pyrrole, quinoline, thiophene, &c. (Meyer and Tanzen, Ber. 46, 3183; Meyer and Wesche, Ber. 50, 422; Tschitschibabin, J. Russ. Phys. Chem. Soc. 47. 702), whilst a 50 p.c. yield of acetonitrile under certain conditions is claimed by the Chem. Fab. Rhenania (E. P. 109983).

According to G. Capellen (Amer. Chem. Abstr. 2, 1562) and O. de Coninck (Bull. acad. roy. Belg. 1908, 303) thiophene is not producible direct from acetylene and sulphur; a good yield, however, of thiophene can be obtained by passing acetylene over pyrites heated to 280°-310° (Steinkopf and Kirchhoff, Annalen, 403, 1; D. R. P. 252375; Fr. Pat. 446136; Austr. P. 72291, 1916; Eng. Pat. 16810, 1912). Tschitschibabin (*l.c.*) claims to obtain a purer product from sulphuretted hydrogen than by Steinkopf's method.

According to the Chemische Fabrik Rhenania (Eng. Pat. 109983) thiophene is produced also by passing acetylene mixed with sulphuretted hydrogen over nickel hydroxide mixed with cement, or better over partially reduced bauxite.

On treating acetylene with hydrocyanic acid (*e.g.* by treating powdered calcium carbide and potassium cyanide with dilute sulphuric acid and evaporating the residue) a 5 p.c. yield of succinic acid is obtained, pointing to the intermediate formation of succinic nitrile:

$$C_2H_2+2HCN = (CH_2CN)_2 \rightarrow (CH_2\cdot COOH)_2$$

(E. Comanducci, Chem. Zeit. 35, 383).

Heinemann (Eng. Pat. 12365, 1913; Fr. Pat. 458,397; U.S. Pat. 1134677) describes the production of propylene by passing a mixture of acetylene and methane over heated contact substances:

$$CH{\vdots}CH+CH_4 = CH_3\cdot CH:CH_2$$

which can then be converted by circuitous routes into glycerine, acetone, &c. A yield of 70 p.c. is claimed using a catalyst consisting of platinum and copper, aluminium or magnesium on pumice at 100°-200°.

By allowing acetone or its homologues to act upon the alkali compounds of acetylene, 3-*methyl-butenol* or its homologues are produced (Farbwerke vorm Fr. Bayer, D. R. P. 285770):

$$(CH_3)_2CO+CH_2\cdot CHNa \rightarrow (CH_3)_2C(OH)C{\vdots}CH$$

According to D. R. P. 280226 and 291185, the same result is obtained by allowing acetone and acetylene to interact in the presence of alkali alcoholates. (*Cf.* also D. R. P. 284764, 286920, 289800.) On reduction the product yields 3-methyl-butenol (D. R. P. 288271):

$$(CH_3)_2C(OH)CH:CH$$

which can then be dehydrated to 2-methyl butadiene (isoprene) and polymerised to synthetic rubber.

(Other possible modes of obtaining synthetic rubber from acetylene are described by Dreyfus in Eng. Pat. 17193, 1913 (void).)

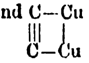
Compounds with metals and metallic salts.

A characteristic property of acetylene and its congeners is their ability to form additive compounds and substitution products with metals and metallic salts. When heated with sodium part of the hydrogen is replaced yielding *sodium acetylide* and carbide C_2HNa and C_2Na_2 (Matignon, Compt. rend. 124, 775; 159, 769; Skosarewsky, J. Russ. Phys. Chem. Soc. 36, 863; Moissan, *ibid.* 126, 302; de Forcrand, Bull. Soc. chim. [3] 13, 996). The sodium compound reacts with alkyl iodides in liquid ammonia at −50° to −30° to form homologues of the acetylene series (Lebeau and Picon, Compt, rend. 156, 1077; *cf.* also Moissan, *ibid* 127, 913).

Similar compounds are known with lithium, potassium, caesium and rubidium (Moissan, Compt. rend. 122, 362; Gunz. *ibid* 126, 1866; Bull. Soc. chim. [3] 15, 756; Compt. rend 123, 1273; Moissan, Compt. rend. 127, 911; 126, 302; 137, 463; 136, 1217).

Of particular interest are the compounds of acetylene with silver and copper which are formed on passing the gas through ammoniacal solutions of cuprous or silver salts; the former compound is a brick-red precipitate of varying composition and is used as a test for the presence of the gas; it appears to have the composition $Cu_2C_2H_2O$ to which Makowka gives the structure $Cu_2\cdot CH\cdot CHO$ (Ber. 41, 824). On heating gently it loses water yielding Cu_2C_2. Scheiber suggests the formulae:

$CH\vdots C\cdot Cu\cdot Cu(OH)$, and



$$\begin{array}{l} C-Cu \\ \| \quad | \\ C-Cu \end{array}$$

for the two compounds (Ber. 41, 3816; Scheiber and Reckleben, Ber. 44, 210).

The silver compound has the formula $C_2Ag_2H_2O$ or $C_2H_2\cdot 2Ag_2O$ and forms a yellowish precipitate. Both the copper and silver compounds explode on heating (*cf.* Berthelot, Ann. Chim. Phys. [4] 9, 385; Blochmann, Annalen, 173, 174; Kuntzmann, Bull. Soc. chim. [3] 6, 422; Alexander, Ber. 32, 2381; Ilosva, *ibid* 2697; Phillips, Amer. Chem J. 16, 340; Scheiber and Flebbe, Ber. 41, 3816; Makowka, Ber. 41, 824; Freund and Mai, Chem. Zeit 1899, 1, 410; Berthelot, Compt. rend. 132, 1525; Keiser, Amer. Chem J. 14, 285; Noyes and Tucker, Amer. Chem. J. 19, 125; Kuspert, Zeitsch. angew. Chem. 34, 453; Silva, Chem. Zeit. 36, 897; Reckleben and Scheiber, Chem. Zeit. 40, 325)

Acetylene also forms double compounds with salts of copper and silver some of which are explosive, *e.g.* $C_2H_2Cu_2Cl_2$; $C_2H_2\cdot 2Cu_2Cl_2$; $C_2H_2\cdot 3Cu_2Cl_2$; $C_2H_2\cdot 2Ag_2O$; $CuSO_3\cdot 2Cu_2C_2$, and so on. (*Cf.* Chavastalon, Compt. rend. 124, 1364; 125, 245; 126, 1810; 127, 68; 130, 1634, 1764; 131, 48; 132, 1489; Hofmann and Kuspert, Zeitsch. anorg. Chem. 15, 204; Söderbaum, Ber. 30, 760, 814; Willgerodt, Ber. 28, 2107: Arth, Compt. rend. 124, 1534; Berthelot and Delépine, Compt. rend. 129, 369; Nieuwland and Maguire, Amer. Chem. J. 28, 1025; Edwards and Hodgkinson, J. Soc. Chem. Ind. 23, 954; 25, 495; British Association Reports, 1904; Alexander, Ber. 32, 2381; Gooch and Baldwin, Zeitsch. anorg. Chem. 22, 235; Keiser, *l.c.*; Manchot, J. Soc. Chem. Ind. 30, 1302; Bhaduri, Zeitsch. anorg. Chem. 79, 355; 76, 419; Llorens, Anales Soc. Espan. fis. quim. 11, 320.)

The use of acetylene has been suggested as an analytical reagent for the separation of metals such as silver, copper, palladium, osmium, gold, and mercury (Söderbaum, Ber. 30, 760, 814, 902, 3014; Erdmann and Makowka, Zeitsch. anal. Chem. 46, 128, 145; Scheiber, Ber. 41, 3816; Scheiber and Reckleben, Ber. 44, 210; Llorens, Anales soc. Espan. fis. quim. 10, 139; 11, 320; Weaver, J. Amer. Chem. Soc. 36, 2462).

For the detection and estimation of acetylene use is made chiefly of ammoniacal cuprous chloride solution. Llorens (*l.c.*) recommends the use of test papers soaked in a solution of copper sulphate and sodium chloride decolorised with sodium bisulphite. Weaver (J. Amer. Chem. Soc. 38, 352) describes a colorimetric method of estimating acetylene. Schultze (Zeitsch. angew. Chem. 29, 1, 341) also describes a colorimetric method. (See also above references on use of acetylene as a reagent.)

With aluminium chloride in presence of alcohol double compounds are formed:

$$AlCl_3\cdot 2C_2H_2\cdot H_2O;$$
$$AlCl_3\, C_2H_2\cdot 2EtOH;$$
$$AlCl_3\cdot C_2H_2\cdot CH_3OH\cdot H_2O$$

(Ganghoff and Henderson, J. Amer. Chem. Soc. 38, 1382; 39, 1420; *cf.* also Band, Chem. News, 81, 286).

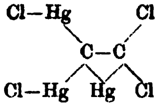
With magnesium bromide compounds are formed such as $CH\vdots CMgBr$, $(\vdots CMgBr_2)$, (Oddo, Atti R. Acad. Lincei. 13, 187; (Gaz. chim. ital. 38, i. 625; Yocichi, J. Russ. Phys. Chem. Soc. 38, 1040).

Action on magnesium, see Novak (Ber. 42, 4209) and Cottrell (J. Phys Chem. 18, 85).

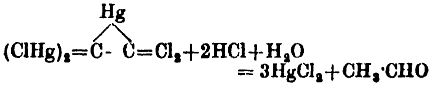
The compounds of acetylene with mercury and mercuric salts have been studied in some detail, and are of considerable importance in view of the use of mercury salts as catalysts for the conversion of acetylene into acetaldehyde. *Mercuric acetylide* (or carbide) itself, C_2Hg, is obtainable as a white very explosive precipitate, by passing acetylene through Nessler solution (Keiser, Amer. Chem. J. 15, 535); on treatment with acids acetylene is evolved. A hydrate, $3C_2Hg\cdot H_2O$, is known also (Plimpton and Travers, Trans. Chem. Soc. 65, 226). A hydrate of mercuro-acetylide, $C_2Hg_2\cdot H_2O$, is formed as a grey precipitate on passing acetylene through an aqueous suspension of mercurous acetate in the dark (Burkard and Travers, Trans. Chem. Soc. 81, 1270). Mercuric acetate solution yields a slimy white precipitate of $3C_2Hg\cdot 2HgO\cdot 2H_2O$ (possibly $3C_2Hg\cdot 2Hg(OH)_2$), which is not explosive and yields acetaldehyde but no acetylene on treatment with acids (Burkard and Travers, *l.c.*; Plimpton, Proc. Chem. Soc. 8, 109).

By the action of acetylene on aqueous mercuric chloride solution an amorphous white precipitate is formed to which the formula $C_2Hg\cdot HgCl_2$ was first given (*i.e.* Bis-chlormercuri-acetylene $ClHg\cdot C\vdots C\cdot HgCl$), but which appears in reality to be *trichlormercuri-acetaldehyde* $(ClHg)_3\vdots C\cdot CHO\cdot$ (Keiser, Amer. Chem. J. 15, 537;

Biginelli, Chem. Zentr. 1898, i. 926; Hofmann, Ber. 31, 2212, 2783; 32, 874; 37, 4459; 38, 663; Biltz and Mumm, Ber. 37, 4417; 38, 133; Annalen, 404, 219; Brame, Trans. Chem. Soc. 87, 427). On heating an aqueous suspension of the compound it is decomposed yielding acetaldehyde in practically quantitative yield (Kutscherow, Ber. 14, 1540; 17, 13; Erdmann and Köthner, Zeitsch. anorg. Chem. 18, 48; *cf.* also Hofmann and others, *supra*; Béhal. Ann. Chim. Phys. [6] 15, 267). According to Hofmann the compound has the structure:

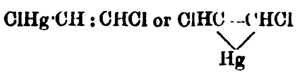


and is formed by the addition of two molecules $HgCl_2$ to one of HgC_2; it is then split up by water:



$$(ClHg)_2{=}C\text{-}C{=}Cl_2+2HCl+H_2O = 3HgCl_2+CH_3{\cdot}CHO$$

More recently Chapman and Jenkins have shown (Trans. Chem. Soc. 115, 847) that on passing acetylene into a saturated solution of mercuric chloride in absolute alcohol a large yield of a white crystalline addition product is obtained which is readily soluble in ether, benzene, and other organic solvents. It has the composition $HgCl_2{\cdot}C_2H_2$, and melts at 113° C. Chapman and Jenkins suggest its formula may be



$$ClHg{\cdot}CH:CHCl \text{ or } ClHC{-}CHCl$$

and it seems probable that this body may be the first product formed during the action of acetylene upon aqueous solutions of mercuric salts. When passed into alcohol in the presence of a mercury catalyst acetal is formed (*v.* ACETALS), and with anhydrous acetic acid ethylidene diacetate is formed which can be readily split up into aldehyde and acetic anhydride (*v.* ACETALS). (See also Hofmann and Kirmreuther, Ber. 41, 314; 42, 4232.)

Acetaldehyde is also formed to some extent by heating charcoal saturated with acetylene to 350° with water (Degrez, Ann. Chim Phys. [7] 3, 216). (For details *see* ALDEHYDES.)

Oxidising agents convert acetylene to acetic acid; thus hydrogen peroxide (Cross, Bevan and Heiberg, Ber. 33, 2015) and fused caustic alkali (Feuchter, Chem. Zeit. 38, 273) yield acetic acid or its salts.

Various processes have been patented, notably by the Farbwerke vorm. Fr. Bayer, to obtain acetic acid direct from acetylene without isolating the acetaldehyde formed as an intermediate product. This process, described in U.S. Pat. 1128780, claims the production of acetic acid by treating acetylene with a mixture formed from mercuric oxide, hydrogen peroxide and ammonium or potassium persulphate in 10 to 30 p.c. sulphuric acid. Fr. Pat. 467515, describing the same process, states that 10·8 grams acetylene yield 24–25 grams pure acetic acid. Fr. Pat. 467778 (D. R. P. 293011; U.S. Pat. 1159376) describes an electrolytic process using 30 p.c. sulphuric acid containing about 1–2 p.c. of a mercury salt at 30° to 40°, with a divided cell using a lead or copper cathode and oxidising the acetylene at the platinum anode; using a current of 48·5 grams acetylene per hour with 100 amps. the yield is stated to be 0·5 kg. acetic acid per litre in 24 hours.

A different process is given by the Chem Fabrik Griesheim Elektron (Swiss Pat 70152 Eng. Pat. 14113, 1914), consisting in passing acetylene and oxygen alternately or simultaneously into acetic or other organic acid containing water to which a suitable mercury catalyst has been added. It does not appear however, to offer much advantage over the methods involving the previous isolation of the acetaldehyde.

HALOGEN DERIVATIVES.

Iodine Compounds.—Acetylene unites with iodine somewhat slowly to form acetylene di-iodide (sym. diiodoethylene) $C_2H_2I_2$, which exists in two stereoisomeric forms, a solid, m.p. 73° (or 78° ?), b.p. 192°; and a liquid form, m.p. 21°, b.p. 185°, $D_{20}=3{\cdot}06$ (Berthelot, Annalen, 132, 122; Sabanejew, Annalen, 178, 118; 216, 275; Plimpton, Trans. Chem. Soc. 41, 391; Paternò and Peratoner, Gazz. chim. ital. 19, 580; 20, 670; Biltz, Ber. 30, 1200, 1207; Nef, Annalen, 298, 341; de Chalmot, Amer. Chem. J. 19, 877; Keiser, Amer. Chem. J. 21, 261; Erdmann, Ber. 38, 237; Chavanne and Vos, Compt. rend. 158, 1582).

With alcoholic potash the liquid form yields acetylene and *di-iodo-acetylene* C_2I_2; chlorine converts it into the tetrachlor derivative. Keiser and McMaster have shown (Amer. Chem. J. 46, 518) that the solid form can be made to yield fumaric acid and therefore has the *trans* form, whilst the liquid *cis* form yields maleic acid.

Di-iodo-acetylene C_2I_2 is formed on treating calcium carbide with a solution of iodine in potassium iodide, tetraiodoethylene being also formed (Biltz, Ber. 30, 1200); or by the action of silver acetylide on an ethereal solution of iodine (Berend, Annalen, 135, 258; Baeyer, Ber. 18, 2275). It can also be produced from tetra-iodo ethylene (Nef, Annalen, 298, 341; Schenk and Litzendorff, Ber. 37, 345) and from iodo-propiolic acid (Nef, Annalen, 308, 325). It is best prepared by the method of Biltz (*l.c.*), by leading acetylene into 2N caustic soda lye into which a solution of iodine in potassium iodide is allowed to drip. Thus obtained it is a white amorphous precipitate which crystallises in needles from ligroin, m.p. 82°. It is an evil-smelling substance with pronounced action on the mucous membrane; it has strong antiseptic properties (Biltz and Küppers, Ber. 37, 4415; Mebert, Archiv. f. experim. Path., etc. 41, 114; Löw, Chem. Zentr. 1899, 1, 214). The action of heat or actinic rays converts it into C_2I_4. With nitrous fumes it yields *nitro-tri-iodo ethylene* $CI_2:CINO_2$ (Meyer and Pemsel, Ber. 29, 1411; Biltz and Werner, Ber. 30, 1200; 33, 2190; Biltz and Küppers, *l.c.*; Chalmot, Amer. Chem. J. 19, 877; Nef, Annalen, 298, 202).

Magnesium acetylene iodide is known and forms a thick oily liquid (Yocichi, J. Russ. Phys. Chem. Soc. 38, 1040).

Bromine Derivatives. *Brom-acetylene* $CBr\vdots CH$ is formed by the decomposition of ethylene dibromide with alcoholic potash:

$$CHBr:CHBr-HBr = CBr\vdots CH$$

It condenses to a colourless liquid, b.p. about −2°. Both liquid and vapour are spontaneously inflammable. It burns with very great energy in air, partially carbonising and forming HBr, CO. and CO_2. Its solutions show phosphorescence and smell strongly like phosphorus. In day light it polymerises, about 10 p.c. of the product being sym. tribrom-benzene (Reboul, Annalen, 125, 81; Schmelz and Beilstein, Annalen, Spl. 3, 280 (1865); Sabanejew, Ber. 18; Ref. 374; Nef, Annalen, 298, 355; 308, 325; Gray, Trans. Chem. Soc. 71, 1029).

Di-brom-acetylene $CBr\vdots CBr$, is formed by treating tribromethylene with alcoholic potash (Lemoult, Compt. rend. 136, 55; 137, 1333; Lawrie, Amer. Chem. J. 36, 490). It forms an oil insoluble in water, possessing an unpleasant isonitrile odour, b.p. 76°–77°. It is very poisonous and is spontaneously inflammable. With bromine it forms *tetra-bromethylene* C_2Br_4, and with iodine it forms dibrom-diodoethylene $BrC:CI_2$, m.p. 95°–96°. Acetylene itself reacts with bromine to form *acetylene dibromide* (dibromethylene) $CHBr:CHBr$, using dilute bromine solutions and keeping the acetylene in excess; the product is a colourless liquid, b.p. 110°, $D_{17}=2{\cdot}271$. It is also produced by the action of zinc and alcohol or amalgamated zinc on acetylene tetrabromide (Sabanejew, Annalen, 178, 115; 216, 251, 267; Ber. 18; Ref. 374; Weger, Annalen, 221, 72; Anschütz, *ibid.* 221, 141; Moureau, Bull. Soc. chim. [3] 21, 99; Elbs and Newmann, J. pr. Chem [2] 58, 246; Swarts, Chem. Zentr. 1899, 1, 589; Gray, 71, 1023). Van de Walle (Bull. Soc. chim. Belg. 27, 209) has shown that acetylene dibromide prepared by the reduction method consists of a mixture of two isomers which can be separated by the fractional distillation of the binary mixtures with ethyl alcohol. The two forms have m.p. −6·5° and −53°, and the equilibrium mixture consists of about one part of the former and two parts of the latter.

If acetylene be treated with excess of bromine the tetrabrom derivative is formed, $C_2H_2Br_4$ (*acetylene tetrabromide, tetrabrom ethane*) (Reboul, Annalen, 124, 269; Sabanejew, Annalen, 178, 112, 121; 216, 255; Bourjoin, Ann. Chim. Phys. [5] 4, 423; Anschütz, Annalen, 221, 138; Wojzic, Ber. 16, 2891; Crossley, Proc. Chem. Soc. 14, 248; Hofmann and Kirmreuther, Ber. 41, 314; Elbs and Newman, J. pr. Chem. [2] 58, 245; Muthmann, Zeitsch. f. Krystallographie, 30, 73). An unsymmetrical tetrabrom ethane is also known (Lennox, Annalen, 122, 124; Sabanejew, Annalen, 216, 255; Anschütz, Annalen, 221, 140).

Perbrom-ethylene C_2Br_4 forms colourless crystals of m.p. 56°, b.p. 226°–7°, and is prepared either by the addition of bromine to dibrom-acetylene (*v.s.*) or by the action of bromine on an aqueous suspension of silver acetylide, and by distilling hexabromethane (Löwig, Pogg. Ann. 16, 377; Lennox, Annalen, 122, 126; Reboul, Annalen, 124, 271; Merz and Weith, Ber. 1[illegible], 2238; Höland, Annalen, 240, 237; Nef, Annalen, 298, 332; Biltz, Ber. 35, 1530). By the action of sodium ethylate tetrabrom ethylene yields asymm. dibrom-vinyl ether, bromacetic ester, tribromvinyl ether, and aldehyde resin (Nef, Annalen, 298, 334). Fuming nitric acid oxidises it to tribrom-acetic acid, or in presence of conc. sulphuric acid tribrom acetyl bromide is formed (Biltz, Ber. 35, 1536).

Various mixed halogen compounds derived from acetylene are also known but are of little importance.

Chlorine Derivatives.—Owing to the cheapness of chlorine its compounds with acetylene are easily and economically produced, and constitute an important technical application of acetylene.

Chlor-acetylene $CCl\vdots CH$ is a gas with explosive properties (Wallach, Annalen, 203, 88; Zincke, Ber. 23, 3783; V. Meyer, Ber. 23, 3783; Hofmann and Kirmreuther, Ber. 42, 4232; Mourelo and Banus, Anales. soc. Espan. fis. quim. 9, 84).

Dichlor-acetylene $CCl\vdots CCl$ has been obtained by Boëseken and Carrière. (Verslag, Akad. Wetenschappen, 22, 1186) by heating the barium salt of trichloracrylic acid:

$$Ba(CCl_2:CCl{\cdot}COO)_2=BaCl_2+2CO_2+2CCl:CCl$$

It is a colourless gas with an unpleasant odour; it can be condensed to a colourless liquid, m.p. −50°, which is explosive. Mixed with hydrogen it inflames spontaneously in the air. It is also possible that dichloracetylene is formed to some extent when calcium carbide is treated with chlorine (Davidson, Amer. Chem. J. 40, 397). For instance, by treatment of benzene with powdered calcium carbide and chlorine, *tolane dichloride* is formed, a reaction best explained by the intermediate formation of dichloracetylene; direct evidence was also obtained that the gas is formed under these conditions.

Acetylene tetrachloride (tetrachlorethane) $CHCl_2{\cdot}CHCl_2$ is the most important halogen derivative of acetylene from a technical point of view, as it is the direct product of the action of chlorine on acetylene and is the starting point for numerous other derivatives. Chlorine is without action on acetylene in the pure state and in the absence of light (Schlegel, Annalen, 226, 154). In diffused daylight the dichlor- and tetrachlor derivatives are formed in succession:

$$C_2H_2+Cl_2 = C_2H_2Cl_2 \quad C_2H_2Cl_2+Cl_2 = C_2H_2Cl_4$$

(Römer, Annalen, 233, 214). Traces of impurities, particularly air (Mouneyrat, Bull. Soc. chim. [3] 19, 447, 452, 454), cause violent explosive decomposition during the reaction, with formation of free carbon and hydrochloric acid:

$$C_2H_2+Cl_2 = 2C+2HCl$$

To avoid this danger and to render the reaction safe and dependable, various devices are adopted chiefly depending upon the presence of suitable catalysts, such as iodine chloride (Sabanejew, Annalen, 216, 241, 262), antimony pentachloride (Berthelot and Jungfleisch, Annalen, Suppl. 7, 252 (1870)), aluminium chloride (Mouneyrat, Bull. Soc. chim. [3] 19, 448; Compt. rend. 126, 1805). For this reason most of the early patents on the subject deal with methods for avoiding the danger of explosion during the reaction and effecting a smooth and continuous combination of the gases. The following processes may be noted: Askenasy and Mugdan (Eng. Pat. 18602, 1904) prepare the sym. tetrachlorethane by passing acetylene and chlorine alternately into antimony pentachloride, which latter should be free from excess of chlorine and may be diluted with tetrachlorethane; or the two gases may be driven in simultaneously into two halves of a vessel separated by a perforated diaphragm. H. K. Tompkins (Eng. Pat. 19568, 1904) advocates the use of a mixture of antimony tri- and pentachloride at 40° to 50° and distilling the product; the reaction appears to be

$$C_2H_2+SbCl_5=C_2H_2{\cdot}SbCl_5$$
$$C_2H_2{\cdot}SbCl_5+SbCl_5=C_2H_2Cl_4+2SbCl_3$$

G. Dreyfus, H. K. Tompkins, and the Clayton Aniline Co. (Eng. Pat. 8438, 1909) describe the production of antimony chloracetylide by passing acetylene into antimony pentachloride. The use of antimony chlor- or brom-acetylides is claimed by Dreyfus, Tompkins, and the Clayton Aniline Co., as a catalyst for use in the production of halogen indigos and thioindigos (*l.c.*).

J. M. Lidholm (Eng. Pat. 22094, 1905) recommends diluting the gases with an indifferent gas such as carbon dioxide and exposing the mixture to actinic rays. Chemische Fabrik Griesheim Elektron (Eng. Pat. 13411, 1907) claim the production of tetrachlorethane by mixing the reacting gases with solid diluents such as sand, infusorial earth, clay, &c., and exposing to actinic rays in presence of the solid. After the gases have been mixed they may be passed into liquids such as the chlorides of antimony or solutions of these in the tetrachlor compound. G. Ornstein (Eng. Pat. 2375, 1911) also advises the use of a non-volatile catalyst such as iron. Salzbergwerk Neu Stassfurth (D. R. P. 174068) suggest the use of sulphur chloride to which a small amount of iron has been added. The Consortium f. Elektrochemische Industrie (Eng. Pat. 25967, 1910) claim that ferric chloride is an efficient catalyst; it is possible that the two preceding patents also depend on the formation of ferric chloride as the real catalytic agent. (*Cf.* also E. P. 132757, Soc. d. prod. chim. d'Alais.)

In practice the use of antimony pentachloride appears to find most favour. The apparatus used consists of a vessel fitted with a stirrer and divided by a partition which, however, allows the intermixing of the liquids. The vessel is partially filled with a solution of antimony pentachloride in tetrachlorethane and acetylene is passed into one side whilst chlorine is led into the other; the acetylene compound is thus continuously formed in the one chamber and decomposed by the excess of chlorine on coming into the other. The vessel gradually fills with the acetylene tetrachloride so formed until a liquid containing as little as 1 p.c. of the catalyst remains. The acetylene is then stopped, a small amount of chlorine is added to decompose the double compound and the tetrachloride is distilled off, purified with lime or chalk and distilled in steam. The yield is about 95 p.c. The process is used in England by the Weston Chemical Co., in France by the Compagnie Générale d'Elektrochemie de Bozel, Paris, and in Germany by the Consortium für Elektrochemische Industrie in Nürnberg, and by the Bosnische Elektrizitäts A.G. in Jajce. The Salzbergwerk Neu Stassfürth make use of Ornstein's process using iron as a catalyst, though probably ferric chloride is the real agent.

Acetylene tetrachloride forms a colourless liquid of b.p. 147°, $D_0=1{\cdot}614$, m.p. −36°. It is the most important of the acetylene halides as it is the mother substance of a large number of derivatives (*v. infra*). Like the latter it is non-inflammable, and as it possesses very great solvent power for organic substances, especially fats, varnishes, &c., it attained to some importance in industry. It is a good solvent for sulphur, phosphorus, and the halogens. It also dissolves acetyl-cellulose and was used for this purpose under the name 'Acetosol' (*cf.* Lederer, D. R. P. 175379; Walker, U.S. Pat. 1035108). It can be distilled unchanged either alone or with steam, and does not attack metals in the dry state. In the presence of moisture, however, certain metals, notably zinc and iron, remove halogen leaving acetylene dichloride. It is stable to strong acids but is readily attacked by alkalis or magnesium hydroxide, yielding trichlorethylene. Heated alone or with $AlCl_3$ or ThO_2 trichlorethylene is formed slowly, and prolonged heating causes the formation also of perchlorbenzene (Berthelot and Jungfleisch, Annalen, Suppl. 7, 252 (1870); Nicodemus, J. pr. Chem. 83, 312).

The Salzbergwerk N. Stassfürth (D. R. P. 185374) recommend the addition of organic compounds such as turpentine to the tetrachloride to take up any hydrochloric acid that may be formed, thus keeping the solvent in a neutral condition suitable for use. A. Schmitz (Fr. Pat. 417649) claims the production of emulsions of tetrachlorethane with soap solutions.

Owing, however, to the strong narcotic and poisonous action of the tetrachloride, causing jaundice, fatty degeneration of the organs, albuminuria and hæmoglobinuria, its use as a solvent is now considerably restricted, particularly as its various derivatives are equally suitable for most purposes and are less poisonous (*cf.* Grimm, Heffter and Joachimaglu, Vrtljschr. Med. Offent. Sanitatsw. 48, 1; Report of H.M. Inspector of Factories, 1914).

Trichlorethylene C_2HCl_3 is obtained from acetylene tetrachloride by heating in a vat with milk of lime or solid lime (Consort. f. Elektrochem. Ind. D. R. P. 171900, 208854). The yield is practically quantitative. It is also produced by passing ammonia into a mixture of acetylene tetrachloride and alcohol (Tompkins, Eng. Pat. 19568, 1904), and, admixed with hexachlorbenzene, by passing the tetrachloride through a tube heated to 400° or 500° (Tompkins and Clayton Aniline Co., Eng. Pat. 23780, 1906). Another process by the Griesheim Elektron Co. (D. R. P. 263457) consists in passing the vapours of acetylene tetrachloride over heated metallic chlorides such as copper or barium chlorides; it is, however, less easy to obtain a pure product by this method. It may also be obtained by passing the tetrachloride over ThO_2 heated to a temperature not exceeding 390° (Chem. Fab. Bückau, D. R. P. 274782).

Trichlorethylene forms a colourless liquid b.p. 85°, $D_0=1{\cdot}47$, which is practically immiscible with water. It has great solvent power for fats, waxes, resins, rubber and other organic products, and also for sulphur and phosphorus, on which account it is used on a considerable scale for fat-extraction and the like in place of benzene or carbon tetrachloride. It has the advantage over acetylene tetrachloride in that it is less toxic (Chem. Zeit. 31, 1095, 32, 256, 529; Arch. Hyg. 1911, 74; Lach, Seifensieder, 1911, 15). Neumann (Chem. Zeit. 35, 1025) states that the trichlor compound gives satisfactory results as a fat solvent (*cf.* also van Lennep and Ruys, Chem. Weekblad, 9, 654). Soaps containing 'Tri' (trichlorethylene) such as 'Westrol,' 'Triol,' 'Tripur,' &c., are used for cleansing textile materials from grease (*cf.* Schmitz, D. R. P. 255901). Trichlorethylene has also advantages over tetrachlorethane in that it is more resistant to chemical action, is unattacked by dilute acids, or by alkalis or lime, and is practically without action on the common metals such as iron, copper, lead, tin, or zinc, even in the presence of moisture. At room temperature it oxidises slowly yielding carbonyl chloride, hydrochloric acid, and dichloracetyl chloride (Erdmann, J. pr Chem. 85, 78; Staudinger, *ibid.* 85, 330). Under suitable conditions it can be made, however, to undergo various important transformations; thus, by heating with strong alkali glycollic acid is formed (Consort. f. Elektrochem. Ind., D. R. P. 257878),

$$\begin{aligned}CHCl:CCl_2+4KOH\\ =CH_2(OH){\cdot}COOK+3KCl+H_2O\end{aligned}$$

Traces of dichloracetylene are also formed. On passing through a heated tube it is partly converted into hexachlorbenzene (Nicodemus, J pr. Chem. 83, 312). In the presence of catalysts chlorine is added on with the formation of pentachlorethane (*v. infra*). On heating with sodium ethylate or a mixture of caustic soda and alcohol, *dichlorvinylether* (dichlorethoxyethylene) is formed (Tompkins, Eng. Pat. 678, 1906; Imbert, Eng. Pat. 5014, 1907), which on further treatment with water or alcohol readily gives chloracetic ester in good yield (Tompkins, *ibid.*)

$$C_2HCl_3+NaOC_2H_5=NaCl+C_2HCl_2{\cdot}OC_2H_5$$
$$C_2HCl_2{\cdot}OC_2H_5+H_2O=HCl+ClCH_2{\cdot}COOC_2H_5$$

According to Imbert (Eng. Pat. 5013, 1907) heating the dichlorethoxy ethylene with the theoretical quantity of water yields the chloracetic ester, whilst excess of water yields chloracetic acid directly. Chloracetic acid or its ester react readily with aniline yielding phenylglycine which can be converted into indigo, thereby offering an alternative route to the usual process starting from acetic acid (*cf.* Chem. Zeit. 35, 1053).

Later processes claim the production of monochloracetic acid in good yields by the use of concentrated sulphuric acid at 150°–200° C., as the hydrating agent (L. V. Simon and G. C. Chavanne, Eng. Pat. 129301), 100 gms. trichlorethylene under such conditions affording 57 gms. monochloracetic acid; the Soc. des prod. chim. d'Alais also describe a continuous process for producing the acid from trichlorethylene by allowing the latter to act upon sulphuric acid of 90 p.c. concentration at 160°–200° C., water being added continuously as required and the resultant monochloracetic acid being carried off by the excess of trichlorethylene (Eng. Pat. 132042).

Dichlorvinyl ether, b.p. 128·2°, $D_{10}=1{\cdot}08$, is an extremely reactive substance opening the way for a number of interesting organic syntheses. Thus hydrochloric acid or chlorine add on directly and the products on distillation split up into chlor- or dichlor-acetyl chloride:

$$\begin{aligned}C_2HCl_2{\cdot}OC_2H_5+HCl&=C_2H_2Cl_3{\cdot}OC_2H_5\\ &=ClC_2H_5+ClCH_2{\cdot}COCl\end{aligned}$$

(*cf.* Tompkins and Clayton Aniline Co., Eng. Pat. 5404, 1908). Chloracetyl chloride made by this process has been placed on the market by the Consortium.

A further use for trichlorethylene is given in Eng. Pat. 90, 1908, by the Badische Anilin und Soda Fabrik, in which by treating trichlorethylene with a salt of thiosalicylic acid, *omega-chlorovinylthiosalicylic acid* is produced which can be readily converted into thioindigo. With mercuric cyanide trichlorethylene yields *mercuritrichlorethylenide* $Hg(CCl:CCl)_2$ (Hofmann and Kirmreuther, Ber. 41, 315).

Dichlorethylene $C_2H_2Cl_2$ is prepared technically from tetrachlorethane by refluxing with zinc dust and water:

$$C_2H_2Cl_4+Zn=C_2H_2Cl_2+ZnCl_2$$

(Askenasy and Mugdan, Eng. Pat. 19576, 1907). Aluminium or iron powders may also be used instead of zinc, but in that case require heating to 140° in an autoclave. The dichloride may also be prepared by the direct union of acetylene and chlorine, avoiding any excess of the latter and using antimony pentachloride as a catalyst (Tompkins) Eng. Pat. 19568, 1904), or diluting the gases and exposing to actinic rays (Lidholm, Eng. Pat. 22094, 1905), or by heating the gases to 150° in capillary tubes (Chem. Fab. Griesheim Elektron, Eng. Pat. 16620, 1912). The commercial product consists of a mixture of the two stereoisomers of b.p. 48° and 60° respectively, and densities 1·265 and 1·291, in consequence of which it has no constant boiling-point (Chavanne, Compt. rend. 154, 776; Bull. Soc. chim. Belg. 26, 287; 28, 234). The equilibrium mixture contains about four parts 'cis' form (b.p. 60°) to one part 'trans' (b.p. 48°) form. Askenasy and Mugdan (Zeit. f. Elektrochemie, 15, 773) suggest the production of the dichloride by electrolysing the tetrachloride in zinc chloride solution, the zinc being regenerated electrolytically.

Dichlorethylene resembles trichlorethylene and perchlorethylene and is unattacked by metals or alkalis. It can be used as a rubber solvent (Fischer, D. R. P. 211186) and owing to its low boiling point has been recommended as a substitute for ether for fat extraction, &c. Its vapour is inflammable but the flame is readily extinguished. (For other details see also Berthelot and Jungfleisch, Annalen, Sppl. 7, 253 (1870); Sabanejew, Annalen, 216, 262.)

Pentachlorethane C_2HCl_5 is prepared by passing chlorine into trichlorethylene, preferably in the presence of actinic rays, from which it is formed in almost quantitative yield; after washing with water and lime to remove excess of chlorine it is distilled in steam and forms a liquid b.p. 159°, D=1·685, and in other respects closely resembles tetrachlorethane (Salzbergwerk Neu Stassfürth, Eng. Pat. 1105, 1912). It has somewhat similar solvent powers to the tetrachlor compound, and is also very sensitive to alkalis, yielding perchlorethylene C_2Cl_4. It does not attack metals in a dry state but does so in the presence of moisture. (For other methods of preparation see Regnault, Annalen, 33, 321; Pierre, Annalen, 80, 130; Paternò, Annalen, 151, 117 Mouneyrat, Bull. Soc. chim. [3] 19, 261.)

Perchlorethylene (tetrachlorethylene) C_2Cl_4: is prepared by treating pentachlorethane with milk of lime; b.p. 119°, D=1·624. Its other properties are similar to those of trichlorethylene. It does not attack metals even in a moist state and is stable to alkalis. It has a certain limited use as a cleaning agent for textiles. It is also a by-product in the manufacture of carbon tetrachloride (*cf.* Faraday, Ann. Chim. Phys. [2] 18, 53; Regnault, Annalen, 33, 325, 333; Geuther, Annalen, 107, 212; 111, 175; Prudhomme, Annalen, 156, 342; Schiff, Annalen, 220, 97; Burgoin, Ann. Chim. Phys. [5] 6, 142; Geuther and Fischer, Zeitsch. f. Chemie, 1864, 269; Geuther and Brockhoff, J. pr. Chem. [2] 7, 102; Goldschmidt, Ber. 14, 929; V. Meyer, Ber. 27, 3160; Besson, Compt. rend. 118, 1347; Mouneyrat, Bull. Soc. chim. [3] 19, 182; Biltz, Ber. 35, 1529). Heating with fuming sulphuric acid yields trichloracetic acid (Prudhomme, Zeitsch. f. Chemie. 1870, 380; Biltz, Ber. 35, 1533).

Hexachlorethane (Perchlorethane) C_2Cl_6 is produced by exhaustive chlorination of the lower chlorinated ethane derivatives (*cf.* Faraday, Ann. Chim. Phys. [2] 18, 48; Regnault, *ibid.* 69, 165; Annalen, 33, 323; Hübner and Müller, Zeitsch f. Chemie, 1870, 328; Mouneyrat, Bull. Soc. chim. [3] 17, 797; 19, 454; *ibid.* [3] 17, 794; Michel, Zeitsch. angew. Chem. 19, 1095). It is also formed on passing chloroform through a red-hot tube (Ramsay and Young, Jahr. d. Chemie, 1886, 628). It occurs as a by-product in the production of carbon tetrachloride (V. Meyer, Ber. 27, 3160), and is formed from carbon tetrachloride by heating to 160° with amorphous arsenic (Auger, Compt. rend. 145, 809), or by passing through a heated tube (Kolbe, Annalen, 54, 147).

It is formed readily by refluxing carbon tetrachloride with aluminium amalgam (Hofmann and Seiler, Ber. 38, 3058), and is also formed by direct synthesis if an electric arc be formed in a chlorine atmosphere (*v.* Boltom, Zeitsch. f. Elektrochemie, 8, 169; 9, 209; Lorenz, Annalen, 247, 245; Zeitsch. angew. Chem. 6, 313; Zeitsch f. Elektrochemie, 8, 203). On a commercial scale it can be conveniently prepared by the exhaustive chlorination of acetylene tetrachloride in the presence of aluminium chloride (*cf.* Mouneyrat, *l.c.*). The Salzbergwerk Neu Stassfürth (D. R. P 174068) claim the production of the hexachlor compound by leading acetylene and chlorine alternately into a heated mixture of sulphur chloride and powdered iron. The same firm also claim a process for chlorinating tetrachloroethane in the presence of an artificial source of light rich in actinic rays (Eng. Pat. 1105, 1912). The penta-chlor compound is formed at the same time and may be separated by allowing the mass to crystallise and then pressing the product.

Hexachlorethane forms colourless crystals melting at 187° to 188°; its b.p. is 185° so that it usually sublimes without melting on being heated. Sp.gr.=2·091. It has a camphor-like odour and is used to some extent in the explosives industry as a camphor substitute in the preparation of safety explosives. Heated with alkali to 200° it yields oxalic acid; nascent hydrogen, alcoholic alkali hydrosulphite, or heating with silver to 280° converts it into perchlorethylene. Heating with antimony pentachloride to 450° converts it completely into carbon tetrachloride (Hahn, Ber. 11, 1735; Schröder, Ber. 13, 1070; Berthelot, Annalen, 109, 121; Geuther, Annalen, 107, 212; 111, 174; Armstrong, J. pr. Chem. [2] 1, 251; Geuther and Brockhoff, J. pr. Chem. [2] 7, 174; Prudhomme, Annalen, 156, 342; Hartmann, Ber. 24, 1023; Gossner, Zeitsch. f. Kryst. 38, 151)

Heated in the presence of water it is converted gradually into perchlor-ethylene.

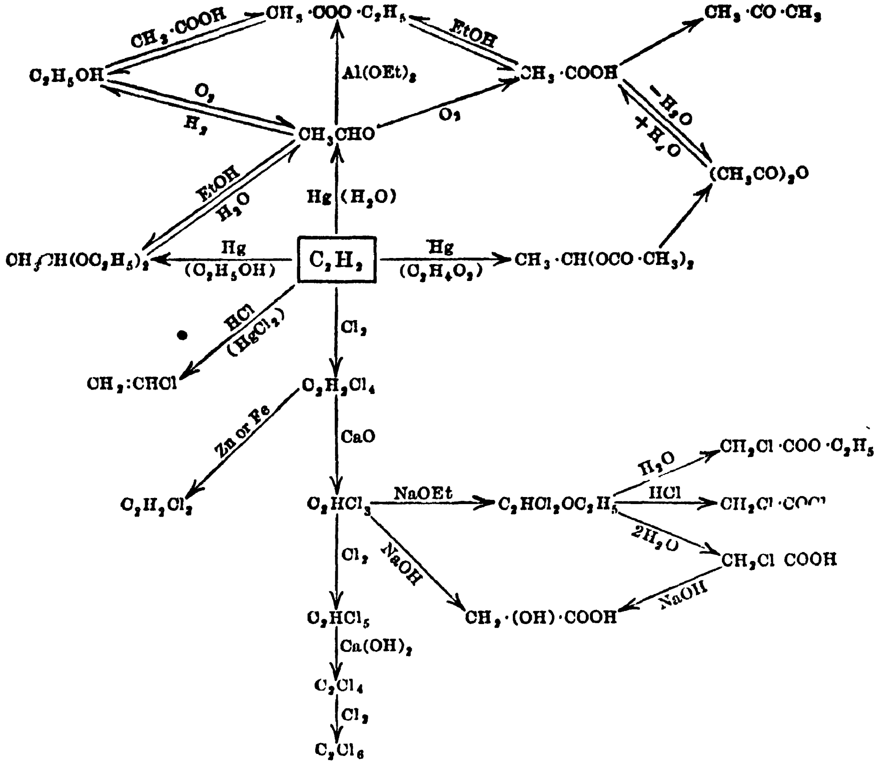
A general discussion of the above chlorinated derivatives of acetylene and their applicability in industry will be found in the following: Chem. Zeit. 31, 1095; 32, 256; 35, 1053; J. Soc. Chem. Ind. 35, 94.

Vinyl chloride (Chlorethylene) $CH_2:CHCl$ is produced by the addition of hydrochloric acid to acetylene in the presence of a suitable catalyst such as pumice soaked in mercuric chloride. Hydrogen chloride and acetylene in molecular proportions are passed through tubes containing the contact mass heated to 180°. The yield is stated to be quantitative (Chem. Fab. Griesheim Elektron, D. R. P. 278249, 288584, Eng. Pat. 21134, 1913). It is a colourless gas which condenses to a liquid in a freezing mixture. It is sparingly soluble in water, readily so in alcohol. In sunlight it polymerises to a transparent white mass (Regnault, Annalen, 14, 28; Wurtz and Frapolli, Annalen, 108, 223; Baumann, Annalen, 163, 317; Glinsky, Zeitsch. f. Chemie, 1867, 676; Villard, Ann. Chim. Phys. [7] 11, 387; Biltz, Ber. 35, 3524). So far it does not appear to have any special technical application.

The diagram on next page may serve to illustrate the chief chemical transformations which acetylene may be made to undergo on a technical scale.

ACETYLENE HOMOLOGUES.

The higher members of the acetylene series are of relatively slight importance. They may be made by the various general methods given for acetylene itself, such as by heating the monohalogen derivatives of the ethylene series with alcoholic potash, &c. They may also be prepared by treating sodium acetylide with alkyl halides in liquid ammonia at −50° to −30° (Lebeau and Picon, Compt. rend. 156, 1077; Picon, *ibid.* 158, 1346). Another general method is described by Schlechter (D. R. P. 253802), who claims the production of dimethyl acetylene and



ethyl acetylene by heating calcium carbide with methyl or ethyl alcohols respectively, under pressure at 60° to 250°, the products obtained depending partly on the temperature:

$$CaC_2+2CH_3OH = Ca(OH)_2+C_4H_6$$

The following members of the acetylene series have been identified as occurring in coal-gas: allylene, ethyl-acetylene, propyl-, isopropyl-, butyl-, isobutyl, methyl-ethyl, and methyl-propyl-acetylenes, and crotonylene (Harzer, J. f. Gasbeleuchtung, 57, 622).

The Chem. Fabrik. Flörsheim (Amer Chem. Abstr. 1912, 1072) state that a general method for the preparation of the dialkyl acetylenes is to heat the monoalkyl acetylenes at 170° with alcoholic potash, the methyl alkyl acetylenes being always formed. The reverse action takes place on boiling with metallic sodium.

Methyl-acetylene, or Allylene, $CH_3·C:CH$, is formed by the action of alcoholic potash on brompropylene:

$$CH_3·CBr:CH+KOH=CH_3·C:CH+KBr+H_2O$$

also by acting with sodium on dichloracetone chloride:

$$CH_3·CCl_2·CHCl_2+4Na = CH_3·C:CH+4NaCl$$

or by electrolysing the alkali salts of citraconic or mesaconic acids, or by the action of magnesium on acetone vapour and treating the solid mass thus obtained with water (Keiser, Amer. Chem. J. 18, 328; Desgrez, Bull. Soc. chim. [3] 11, 391; Lespieau and Chavanne, Compt. rend. 140, 1035).

Allylene is a colourless gas, b.p. −23·5°; m.p. −100°; very similar to acetylene and, like it, forming compounds with metals. The mercuric compound $(C_3H_2)_2Hg$ is obtained by passing allylene through water containing mercuric oxide in suspension. It crystallises from hot alcohol in fine needles. It is soluble in hydrochloric acid with evolution of allylene, but does not explode on heating (Keiser, *l.c.*; Lossen and Dorno, Annalen, 342, 187; Plimpton and Travers, Chem. Soc. Trans, 1894, 264; Biltz and Mumm, Ber 37, 4417; Hofmann, Ber 37, 4459). The silver compound $(C_3H_2)_2Ag$ forms microscopic needles which explode at about 150°.

According to Berthelot (Compt. rend. 126, 561, 567, 609, 616) allylene when subjected to the silent electric discharge condenses to a solid with a pungent empyreumatic odour; with nitrogen the substance $C_{15}H_{20}N$ is formed.

Allylene forms with bromine additive products, $C_3H_4Br_2$ and $C_3H_4Br_4$, and with halogen acid compounds of the type $CH_3·CCl_2·CH_3$. Concentrated sulphuric acid absorbs allylene readily, and on distilling the solution with water, acetone, mesitylene and allylene sulphonic acid, $C_3H_3SO_3H$, are formed (Schrohe, Ber. 8, 18, 367). With hypochlorous and hypobromous acids, allylene forms dichlor- and dibrom-acetones, and trimethyl allylene yields the halogen pinacolins (Wittorf, Chem. Zeit. 23, 695).

Butines.—1. *Ethyl acetylene* $C_2H_5·C:CH$. Formed by the action of alcoholic potash on $C_2H_5·CCl_2·CH_3$ (Bruylants, Ber. 8, 412) by passing acetylene and ethylene through a red-hot tube (Berthelot, Ann. Chim. Phys. [4] 9, 466) from dibrom-butane by the action of alcoholic potash (Dupont, Compt. rend. 148, 1522).

The compound is a liquid boiling at 18°, and forms precipitates with ammoniacal copper and silver solutions; f.p. −130°.

With ammoniacal silver chloride and alcoholic silver nitrate it forms explosive compounds (Wislicenus and Schmidt, Annalen, 313, 221); it also yields a sodium derivative (Jociez, Chem. Zentr. 1897, i. 1012).

2. *Crotonylene* or *dimethylacetylene* $CH_3{\cdot}C{:}C{\cdot}CH_3$ is formed by acting with alcoholic potash on βγ-dibrombutane $CH_3{\cdot}CHBr{\cdot}CHBr{\cdot}CH_3$; by the action of sodium ethoxide on monobrompseudobutylene $CH_3{\cdot}CBr : CH{\cdot}CCH_3$ (Hölz, Annalen, 250, 230); or by the decomposition of the salts of β-bromoangelic acid (Wislicenus and Schmidt, *l.c.*). With bromine it forms a product $C_4H_6Br_4$, which is solid, m.p. 243°; isocrotonylene dibromide, b.p. 149° to 150°, is also known and is not readily attacked by zinc dust (Wislicenus and Schmidt, *l.c.*).

Crotonylic mono- and hydro-bromides, as well as the iodide and chloride derivatives, have also been obtained (Wislicenus, Talbot and Henge, *l.c.*; Peratoner, Gazz. chim. ital. 22, ii 86; Charon, Ann. Chim. Phys. 1899, 17, 228; Favorsky, J. pr. Chem. [2] 42, 143).

On shaking the hydrocarbon with sulphuric acid and water (3 : 1), *hexamethyl benzene* is obtained,

$$3C_4H_6 = C_{12}H_{18} = C_6(CH_3)_6$$

The compound $CH{:}C{\cdot}C{:}CH$, formed by the action of cupric chloride on copper acetylene, is described by Noyes and Tucker (Amer. Chem. J. 19, 123); pentachlorbutine C_4HCl_5 by Zincke and Kuster (Ber. 26, 2104). Derivatives of the butines, some of which are used as dyestuffs, are described by Freund (Ber. 34, 3109).

Pentines, C_5H_8, *n-Pentine*, prepared by Picon by the action of propyl iodide on sodium acetylide in liquid ammonia, is a liquid of b.p. 40°, and m.p. −95° (Picon, *l.c.*).

Isopropyl acetylene, prepared by the action of alcoholic potash on the dibromide of isopropylethylene or methyl-ethyl-ethylene, b.p. 115° (Kalinine, J. Russ. Phys. Chem. Soc. 38, 1042). In presence of aqueous solutions of cadmium or zinc chlorides at 150° it is converted quantitatively into methyl propyl ketone (Kutscherow, Ber. 42, 2759).

On treating diallyl-tetrabromide with potash a liquid *dibromodiallyl* is obtained, which boils at 210° and by the action of alcoholic potash this yields *dipropargyl* C_6H_6, a liquid boiling at 85° and isomeric with benzene, but having the constitution,

$$CH{:}C{\cdot}CH_2{\cdot}CH_2{\cdot}C{:}CH$$

Isopropenyl acetylene $CH_2=C(CH_3)-C{\equiv}CH$ forms a liquid, b.p. 67–69°, nD_{20} 1·4332, and is obtained by dehydration of 3-methylbutinol (*v.s.*) by means of anhydrous magnesium sulphate at 230° C. (D.R.P. 290558, Fr. Bayer & Co.). It gives a white precipitate with ammoniacal silver nitrate and a yellow precipitate with ammoniacal cuprous salts. It is of some interest owing to its close relationship with isoprene.

F. A. M.

ACETYLENE—COMMERCIAL APPLICATIONS. Although acetylene was discovered by Davy as far back as 1836, its use as an illuminant became practicable only in 1892, when Moissan in France, and T. L. Willson at Spray, showed that it was possible to make calcium carbide on a commercial scale in the electric furnace. (*See* CALCIUM CARBIDE.)

Calcium carbide, as made in the electric furnace, is a dark crystalline substance with a metallic lustre, having a density of 2·22. The pure compound, however, has been produced by Moissan in thin white semi-transparent plates, the colour of the commercial material being due to the presence of iron and other impurities.

Water decomposes the carbide with reproduction of lime and generation of acetylene:

$$\underset{\text{Calcium carbide}}{CaC_2} + \underset{\text{Water}}{2H_2O} = \underset{\text{Slaked lime}}{Ca(HO)_2} + \underset{\text{Acetylene}}{C_2H_2}$$

In the early days of carbide manufacture little attention was paid to the purity of the materials, with the result that the carbide formed contained impurities, some of which were decomposed by water and gave products contaminating the acetylene. Since the importance of purity in the acetylene has been recognised, everything possible is now done to reduce such impurities to a minimum.

The impurities found in commercial carbide may be divided into those which can be decomposed by water, and those on which water has no action. Amongst the former are substances evolving phosphorus compounds on contact with water, aluminium sulphide, organic sulphur compounds and metallic nitrides: whilst the latter class contains such bodies as graphite, carbides of boron and silicon, carbides and silicides of various metals contained in the lime and in the ash of coke, these being left with the lime residue after the decomposition of the carbide by water, and in no way influencing the purity of the gas.

The purity of commercial acetylene depends primarily on the purity of the carbide from which it is generated, and as long as it is impossible to get absolutely pure materials for the manufacture of the carbide, so long will impurities be found in the gas made from it. The most important of these impurities are:

(*a*) Phosphoretted hydrogen, obtained from the decomposition of calcium phosphide, &c., by water, and, in burning with the acetylene, gives rise to phosphorus pentoxide, which forms a slight haze in the room in which the gas is being burnt.

(*b*) Sulphuretted hydrogen, formed by the action of water on aluminium sulphide, &c., and yielding when burnt sulphur dioxide, which if dissolved by condensing moisture will absorb oxygen from the atmosphere, forming traces of sulphuric acid.

(*c*) Ammonia, from the magnesium nitride, which rapidly corrodes brass gas-fittings, and on burning produces traces of nitrogen acids.

Siliciuretted hydrogen is also found in small quantities in crude acetylene.

Several processes have been devised for the purification of acetylene by the removal of these compounds as well as of the hydrocarbon vapours formed by the polymerisation of the gas due to high temperature during generation. The only impurity that offers any real difficulty in removal is the phosphoretted hydrogen, and three substances have been suggested and used in practice for this purpose: (*a*) bleaching powder, (*b*) acid copper or iron salts, and (*c*) acid solution of chromic acid.

The bleaching powder is employed in the form of small lumps, as offering the least resistance to the flow of the gas when in a slightly moistened state. Its action is purely that of oxidation, the phosphoretted and sulphuretted hydrogen being converted respectively into phosphoric and sulphuric acids, the acetylene being unaffected. To obtain as large a surface as possible the bleaching powder is sometimes mixed with an inert body, such as sawdust or oxide of iron, but in whatever condition the bleaching powder is used the gas requires an after-purification for the elimination of chlorine compounds, for which purpose a lime purifier is generally employed.

Bleaching powder, though an efficient purifying agent when in good order, is apt to be uncertain in its action, and cases have frequently occurred of spontaneous firing and explosion when air has been admitted to purifiers containing this material that have been in use for some time, so that precautions are necessary when using this method of purification.

An acid solution of cuprous chloride, or solids made by impregnating kieselgühr or similar porous bodies with the acid copper salt, are also very effective in removing the various impurities, the phosphorus and sulphur compounds being transformed into copper phosphide and sulphide. The disadvantages of the process are that a second purification with lime is required to remove acid vapours, and that the material being highly acid cannot be used in ordinary metal containers, whilst if the copper salt became neutralised by ammonia there might be danger of the explosive copper acetylide being formed. Under suitable conditions 1 kilogram of the material will purify 20 to 25 cubic metres of the gas, the acetylene not being acted upon, and the action being regular and certain.

Chromic acid in solution containing sulphuric or acetic acid, or kieselgühr charged with this mixture, is the third purifying agent, and eliminates the phosphoretted and sulphuretted hydrogen and the ammonia. When exhausted the spent material can be regenerated by exposure to the air.

In practice these three materials seem to give equally good results, and the passage of the gas through the solution or solid scrubs out of it to a great extent the tarry fog and lime dust often mechanically held in the gas when it has been generated too rapidly or at too high a temperature.

Absolute purification is by no means necessary; for ordinary use all that is required being to reduce the amount of impurity below the limit at which the products of combustion are injurious to health or cause haze; and with a fairly pure specimen of carbide mechanical scrubbing is sufficient if a generator of the non-automatic type is employed, and the gas is stored in a holder before use.

Although the generation of acetylene by bringing calcium carbide in contact with water seems so simple, yet in actual practice it was complicated by several difficulties, amongst which may be mentioned the heat of the reaction, which caused the polymerisation of some of the acetylene, and by the fact that the evolution of gas did not cease immediately the water supply was cut off, this being due to water mechanically held in the residue formed, to the dehydration of the calcium hydroxide by the unchanged carbide, as well as to the moisture condensed from the gas as the temperature of the generator fell.

Acetylene generators.—These can be divided into two main classes—those in which water is brought in contact with the carbide, the latter being in excess; and those in which the carbide is thrown into water, the water being always in excess. The first class may be subdivided into those in which water is allowed to rise to the carbide, those in which it drips on to the carbide, and those in which a vessel full of carbide is lowered into water and then withdrawn as the generation of the gas becomes excessive.

Each of these types may be 'automatic' or 'non-automatic.' In the former are to be found devices for regulating and stopping at will the generation of the gas within limits, whilst the 'non-automatic' variety aim at developing the gas from the carbide with as little loss as possible and storing it in a holder.

The points to be aimed at in a good generator are:

(*a*) Low temperature of generation.

(*b*) Complete decomposition of the carbide.

(*c*) Maximum evolution of gas from carbide used.

(*d*) Low pressure in every part of the apparatus.

(*e*) Removal of all air from the apparatus before collection of the gas.

Generators of the 'drip' type, in which water is allowed to fall slowly upon a mass of carbide, possess most of the disadvantages due to heat of generation, fluctuation of pressure, &c., and this type has been abandoned except for the smallest forms of portable generator. Those in which water rises to the carbide are most efficient, and overheating can be avoided by ensuring that the water never rises above that portion of the carbide which is undergoing decomposition: in other words, that the gas leaves the carbide immediately upon its formation and passes away to the holder with the least opportunity for becoming overheated by contact with decomposing carbide.

Generators in which the carbide dips into water and is then withdrawn are apt to overheat to a dangerous extent, especially if the generator be over-driven.

Although it might be expected that the dropping of the carbide into an excess of water would produce the coolest and purest gas, yet evidence of overheating of the gas is often found in generators of this class, as a coating of lime can form around the lumps, preventing the free access of water, and allowing the interior of the mass from which generation is proceeding to become heated to redness; the efficiency also is lowered as a certain amount of the gas is dissolved in its upward passage through the large volume of water.

Theoretically 64 parts by weight of carbide require only 36 parts by weight of water for complete decomposition and conversion of the lime into hydroxide, but it is found in practice that, owing to the heat of the reaction driving off some of the water as steam, and a further portion mechanically adhering to the slaked lime, double this amount of water is necessary, and the only safe way to ensure entire decomposition of the carbide is to add sufficient water to flood the residue.

Carbide is also supplied in the form of 'briquettes,' coated with material to prevent deterioration in air; at the same time the after-generation of gas when the water supply is stopped is largely prevented. These briquettes are particularly suited for motor car headlight outfits and table lamps.

Combustion of acetylene.—When acetylene is burnt in air under such conditions as to complete its combustion, it is converted into carbon dioxide and water vapour, the same compounds that are produced by all combustible hydrocarbons, 1 cubic foot of the gas requiring 2½ cubic feet of oxygen, or five times that amount of air.

When acetylene was first used for illumination, burners of the Union jet type (similar to coal-gas burners) were employed, some of these being of specially small size. In such burners the orifices for the issue of the gas were very small, and were drilled at a more obtuse angle than for coal gas. Burners of this type, whilst giving good results for a time, soon developed a smoky flame, a filiform growth of carbon appearing on the jet, so that they were generally unsuitable.

Smoking is very likely to develop with acetylene, especially when the gas is turned down. This is due principally to the polymerisation of the gas by heat, producing liquid hydrocarbons (principally benzene) and solid carbon by decomposition, when the gas issuing from the small orifices becomes unduly heated. With a high efflux velocity sufficient air will be drawn in to ensure primary combustion close to the orifice and the trouble is largely overcome, but the reduction of the gas pressure prevents this action. An accumulation of particles of carbon, or other foreign matter, such as lime particles from the generator, will act similarly by impeding the gas flow, so that once carbon begins to form the actions leading to smoking rapidly accelerate.

On breaking open a steatite jet of a burner in which smoking has developed carbon deposit will be found to have extended to some depth, showing that a liquid hydrocarbon has soaked into the steatite and been there further decomposed by heat.

The actions leading to the formation of the liquid product in general arise at the jet, but with a bad type of generator, where overheating takes place, polymerised products may be carried forward in the gas, and deposited in and around the narrow orifice in the steatite or other porous material.

Attempts to overcome these difficulties were on the lines of introducing air, either admixed with gas, which was soon abandoned on account of danger, or constructing the burner so that air was drawn in through adjacent orifices by the injector action of the issuing gas, a method adopted by Bullier (1896-97).

Bullier's principle of making the tips of the burner jets into small bunsens was adopted by Dolan in America, and Billwiller on the Continent.

The Billwiller burner has two steatite arms rising at right angles from a common base from which the acetylene issued at two small orifices exactly opposite each other and giving the double jet. Immediately above the gas orifice a small platinum plate was fixed at a distance of about 0·5 mm. from the steatite, with a hole in it rather larger than the orifice in the steatite just below. The acetylene issuing from the hole in the steatite rushed through the hole in the platinum above and drew air in under the platinum plate. The air so drawn in flowed to the confines of the rapidly travelling stream of acetylene and passed upwards around it, so preventing contact between the edge of the hole in the platinum and the acetylene, whilst the metal, being part of a collar of platinum fixed round each steatite arm, and being a good conductor of heat, prevented such heating as would lead to the deposition of carbon from the gas.

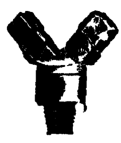


FIG. 1.

In 1897 Dolan in America made a burner on the same principle as the Billwiller burner, though of slightly different construction. It consisted of a metal base, the upright from which forked into two arms, which near their extremities were bent inwards at right angles. These arms carried steatite or 'lava' tips, bored with a fine hole from the interior to the base of the mushroom head, where its diameter was more than doubled, whilst four small lateral air tubes were bored at regular intervals from the base of the head to the broad aperture of the nipple, with the result that the flow of acetylene from the narrow into the wider tube sucked air in through the side tubes and surrounded the ascending gas with an envelope which prevented its contact with the heated tip. These burners, which are more generally known as the 'Naphey' burners, gave very good results, and have been more widely adopted than the Billwiller burners that preceded them, partly because they did away with the expense of the platinum, were cheaper to make, and were less liable to break.

The great drawback to all the Naphey tip burners is that the heat from the flame causes a slight and gradual warping of the metal mounting, with the result that after a time the jets become slightly thrown out of their true position, which at once distorts the flame and causes it to throw up smoky points. This trouble is not found with burners having steatite or composition arms, as these, being pressed or cut, do not warp with the heat.

These burners proved the forerunner of a host of others in all of which the same principle was adopted, one of the simplest and most popular being shown in Fig 2, whilst Fig. 3 is a section of the same burner, showing the construction and air inlets.

Although these burners possess many advantages and can be used for several hundred hours without smoking, they have the drawback that the flame cannot be turned down, as, after the flame has been left turned down for an hour or two, it will be found that it will generally start smoking when the normal consumption is restored.

In order to overcome this trouble Bray introduced a burner in which, by placing a second air-supply chamber of larger dimensions above the first, such a complete encircling of the jet of gas by air was ensured that the variations in gas pressure caused by turning down the flame do not lead to carbonisation.

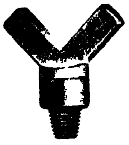


Fig. 2.

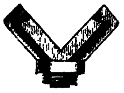


Fig. 3.

Another burner has been brought out in which the idea of air injection has been successfully adapted to a slit burner: the gas issues from a series of fine holes placed below a cap provided with a broad slit and side air tubulure, the gas drawing in sufficient air in its passage through the slit to prevent smoking or carbonisation of the burner (Fig. 4). Such slit type burners are particularly suited for use in motor-car headlights, &c. With twin jet burners an obstruction in one orifice may cause a somewhat long flame to issue from the other orifice, which may impinge on lenses or mirrors situated close to the burner. The slit type is free from this disadvantage.

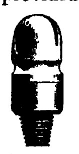


Fig. 4.

From the earliest introduction of acetylene attempts have been made to utilise it with incandescent mantles, but under the pressures which are usually obtained from the ordinary generating apparatus this has not proved successful. Acetylene, when consumed in an atmospheric burner, gives an excessively hot flame, not only on account of its composition, but also from its endothermic character. Several difficulties, however, are met with in trying to burn acetylene mixed with air in sufficient proportion to yield a non-luminous flame, namely:

(*a*) The wide range over which such mixtures are explosive.

(*b*) The low temperature of ignition.

(*c*) The high speed at which the explosive wave travels through the mixture of gas and air.

In order to make a bunsen burner for acetylene the tube has to be very narrow, and even then flashing back is very liable to occur, whilst a high pressure is needed to bring about a satisfactory mixture of the gas with sufficient air to ensure combustion with an absolutely non-luminous flame. The range of explosibility lies between 3 p.c. and 82 p.c. of acetylene in the mixture, and the propagation of the explosive wave cannot be stopped by the ordinary device of using wire gauze, on account of the low ignition point of the mixtures. By using a tube ½ mm. in diameter the explosion ceases to be propagated at all, but such tubes, on account of their small diameter, cannot be utilised singly. The difficulty can be surmounted by using a bundle of small tubes united to form a single burner, or by employing a large tube having a constriction at one point of not more than 5 mm. diameter. The diameter of the tube at the constriction must be in a definite proportion to the particular mixture of air and acetylene consumed, as the more air the greater must be the constriction in the strangulated portion of the tube, owing to the increased velocity of the explosive wave.

With an acetylene bunsen, and using a Welsbach No 2 mantle, as much as 90 candles per cubic foot of acetylene has been obtained. It may be taken that when used with a mantle acetylene will give double the illuminating power per cubic foot as compared with the light obtained when the gas is burnt in the ordinary acetylene flat-flame burners under the best conditions, but very widely different results have been obtained, owing to irregularities in the pressure or lack of air regulation, and at the moment of lighting or turning out there is a liability of a small but violent explosion, which has disastrous effects upon the mantle. A further difficulty is caused when phosphoretted hydrogen is present as an impurity, for this leads to the formation of fusible phosphates of thorium and cerium, with consequent destruction of the mantle. Apart from these considerations, the mantle appears to be hardened and strengthened by the intense heat to which it is subjected, but it is not yet determined how the life of the mantle is affected by the temperature of the flame.

Under the light yielded by the combustion of acetylene colours appear practically the same as in daylight, and all tints and shades can be as clearly distinguished from one another as in sunlight. For this reason the gas has been found to be of invaluable utility in dyeing and colour printing. The spectrum of acetylene, however, although the same as that of daylight for red and yellow, has an increase in the blue rays of 0·46, which brings them to about the same value as the Northern Light. The violet rays show a slight increase, so that acetylene is even richer than sunlight in the rays which are so essential to the chemical action of light, and yet the red rays which are so detrimental in colour work do not predominate, as in the electric arc.

Acetylene has been found of great service in the illumination of small towns and country villages, and for isolated houses and farms. It has been employed in photography on account of its richness in actinic rays. For headlights on motors, for train lighting, for buoys, and in fact in a number of cases where bright and trustworthy light is required without the complication of a coal-gas works or the dangers of oil, acetylene has proved its worth.

It has been found that the rays from an acetylene light possess remarkable penetrative powers in fog or mist, being in this respect superior to the arc light or incandescent mantle.

Storage of dissolved Acetylene.—In the early days of the development of acetylene for commercial purposes attempts were made to employ it in a liquefied form or compressed, but under pressure the gas proved too dangerous. Even at 2 atmospheres pressure acetylene free from oxygen can be exploded. It was enacted in 1807 that the gas should never be subjected to a pressure exceeding 100 inches of water (about 4 lbs. per square inch); later this was raised to 250 inches.

In 1896 Claude and Hess, in France, suggested the idea of making use of the solubility of acetylene in certain liquids as a means of storing this gas, and acetone was tried as the solvent. Acetone dissolves 24 times its volume of acetylene at 15° and under ordinary atmospheric pressure, the solubility increasing proportionately with pressure. The volume of the acetone also increases very largely. It was found that the simple solution of acetylene in acetone, although less liable than the compressed or liquefied acetylene to explosion, could not be said to be sufficiently free from danger to admit of its general use. Janet and Fouche discovered that when acetylene is dissolved in acetone absorbed by porous material of the right kind under 10 atmospheres pressure, it was impossible to produce explosion. The practice in this country for the storage of acetylene is to fill a cylinder with porous material (porosity about 80 p.c.), then to add a volume of acetone equal to 40 p.c. of the original cylinder volume, and pump in the gas to a pressure of 150 lbs. per square inch. In 1901 this was fixed as the legal pressure limit. Thus a cylinder of 1 cubic foot capacity containing 0·4 cubic foot of acetone will hold 100 cubic feet of the gas, most of which will be given off when the valve is opened.

There are practically only three porous materials in use for absorption of dissolved acetylene in the United Kingdom: (*a*) a porous agglomerate of asbestos, kieselguhr, and charcoal, and a suitable cement; (*b*) charcoal filling; (*c*) kapok filling. The porosity should not exceed 80 p.c. The solvent must not completely fill the porous material under any rise of temperature likely to be experienced. With the present type of cylinder, the pressure at present allowed, *i.e.* 150 lbs. per sq. in., should not be increased; for solid drawn cylinders and for those of 100 cubic feet capacity and over in which the acetylene-welding at the top and bottom is strengthened, the pressure allowed might safely be increased to 225 lbs. per square inch provided a solvent is used in addition to the porous material. The best material for the construction of cylinders is a mild steel of high ductility, of which the carbon content does not exceed 0·25 p.c. and the phosphorus and sulphur each do not exceed 0·05 p.c. The test pressure should be four times the working pressure and should be maintained for not less than fifteen minutes (Home Office Report, J. Soc. Chem. Ind. 1918, 116*A*).

Acetylene Welding and Metal Cutting.—Acetylene is largely employed for autogenous welding and for metal cutting; in the latter case extra oxygen being supplied so that the metal itself is burnt away. The temperature of the oxy-acetylene flame is approximately 3000°, and from the nature of the combustion the flame has a reducing action tending to exclude the possibility of oxidation of the metals undergoing treatment. Theoretically 2·5 volumes of oxygen are required for each volume of acetylene, but in practice it is found that the proportions are approximately 1·4 to 1·0, this low proportion of oxygen ensuring a reducing action in the flame.

There are two systems of operating: in the high-pressure system the oxygen is delivered from an ordinary cylinder under pressure, and the acetylene, dissolved in acetone under pressure, is also supplied from cylinders. Both cylinders are fitted with special governors, as a perfect regulation of the flame is one of the main conditions of success. This system has the great advantage of a portable outfit, and can be applied in confined spaces, but it is more expensive than the alternative system.

With the low-pressure plant the acetylene is made in an ordinary generator, which may be of the automatic or non-automatic type, the size of the works to a great extent influencing the kind of generator used, but, whatever type be adopted, it is necessary that the generation of the gas should not be accompanied by overheating, as this leads to low temperatures at the burner and other troubles. The gas should be purified before use, as the presence of the phosphoretted and sulphuretted hydrogen would tend to spoil the weld, and the purifying agent should be renewed when necessary. After leaving the purifiers the gas is distributed to the various points in the workshops in gas- or steam-barrel piping, and at each point a hydraulic back-pressure valve is inserted, in order to prevent the oxygen through any mischance flowing back through the acetylene service. The use of an efficient water-trap is a sufficient safeguard in practice.

The first successful blowpipe was the Fouche, employed with the low-pressure system, and this type has held its own in spite of the competition of other patterns. After the weld has been made the plate is annealed, this being essential. Although the results of tests up to the present are not very consistent, it may be taken that, on the average, the welded joint has a tensile strength from 95 to 80 p.c., depending on the thickness of the plate.

There are many classes of work in which oxy-acetylene welding can be advantageously employed. In the motor-car industry, both in the garage and repair shop, it has proved of great service, it being a comparatively simple matter, for instance, to mend a cracked cylinder or gear-box. For the welding of tubes, repairs to boilers *in situ* needed by corrosion, &c., for the mending of fractured stems and stern posts, the process has been invaluable.

Iron and steel (including thick armour plate) are now commonly cut with oxy-acetylene blowpipes with great saving in time and cost. The method is not so suitable for cast-iron. The blowpipes are made with a central oxygen supply jet, the acetylene serving to heat the metal to its ignition point, when the excess oxygen burns it to oxide, which flows away in a molten condition. The ratio of acetylene to oxygen employed varies from 25 p.c. for thin plate to 10 p.c. for the thickest. The following rates of cut and oxygen consumption are attained:—

Thickness of plate.	Foot run of cut per hour.	Oxygen consumed per ft. run.
1	40	2·2
3	20	9·0
6	18	28·0
9	16	60·0
12	16	100·0

Acetylene for Power Purposes.—Owing to the violence of the explosion when mixed with air acetylene is liable to give unduly high pressures in the cylinders of internal combustion engines. Moreover, it is too expensive to compete with other fuels. Tests on engines of a few horse-power have shown consumptions of about 6·3 cubic feet per B.H.P. hour. It has, however, been successfully employed, particularly in the United States, for starting up motor car engines, the advantage of the gas for this purpose is obvious where it is carried in the compressed form (in acetone) for the usual lighting sets. The violence of the explosion has to be guarded against, otherwise damage to the engine may result. J. S. S. B.

ACETYLSALICYLIC ACID *v.* SALICYLIC ACID.

ACHRODEXTRIN *v.* DEXTRIN.

ACHYRANTHES ASPERA or *Aghara.* An Indian plant used as a simple and as a remedy for toothache.

ACID ALBUMEN *v.* PROTEINS.

ACID ALIZARIN, -BLUE, -GREEN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ACID CERISE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

ACID GREEN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

ACIDIMETRY and ALKALIMETRY. This branch of quantitative analysis dealing with the estimation of acids and alkalis is of great technical importance. In pure aqueous solutions the amount of acid or alkali can usually be ascertained with considerable accuracy by determining the specific gravity of the liquid at a definite temperature and referring to a table especially drawn up for this purpose.

Direct estimations may also be made by suitable gravimetric methods, but volumetric processes are almost exclusively employed, and are indeed the only methods available for distinguishing between free and combined acid or alkali. In these operations the quantity of acid or alkali present is calculated from the amount of standard alkali or acid required respectively to neutralise it exactly, the precise point of neutralisation being determined by the addition of a small quantity of an *indicator*, *i.e.* a substance which by undergoing a marked change of colour renders evident the transition from acidity to alkalinity, or *vice versâ*.

Indicators. Although many natural and artificial colouring matters have been recommended as indicators, comparatively few are actually used, those most frequently employed being *methyl orange*, *phenolphthaleïn*, and *litmus.*

Artificial indicators are either very weak organic acids or (more rarely) weak bases, and the prevalent view regarding their behaviour is that in solution their colour in the non-ionised state differs from that which they exhibit in the ionic condition.

In accordance with the ionic theory of solution, a very weak acid HM exists in solution, mainly, but not entirely, in the non-ionised state, the equilibrium between ions and undissociated molecules $HM \rightleftharpoons \overset{+}{H} + \overset{-}{M}$ being expressed quantitatively by the equation

$$\overset{-}{M} \times \overset{+}{H} / HM = \text{constant}$$

in which the symbols denote the molecular concentrations of the ions and molecules, and where as in the case under discussion $\overset{-}{M}$ and $\overset{+}{H}$ are very small in comparison with HM.

Any increase in the value of $\overset{+}{H}$, which is effected by adding a small quantity of a fairly strong (ionised) acid to the solution, leads to a corresponding diminution in the value of $\overset{-}{M}$. The reverse change, leading to an increase in the value of $\overset{-}{M}$, with a corresponding decrease in the value of $\overset{+}{H}$, is effected by adding a slight amount of a fairly strong (ionised) alkali hydroxide, since the equilibrium $\overset{+}{H} \times \overset{-}{OH} = \text{constant}$ obtains in aqueous solutions, and the alkali added increases considerably the value of the factor $\overset{-}{OH}$. If the acid HM and the ion M differ in colour, then, in any solution containing this acid a change from acidity to alkalinity, *i.e.* from a state in which $\overset{+}{H}$ predominates over $\overset{-}{OH}$ to the reverse condition, may be indicated by an appreciable change of colour. The degree of ionic dissociation of the indicator HM must, however, be considerably smaller than that of either acid or alkali employed in the titration; moreover, another acid HR, having a smaller degree of ionisation than HM, will indicate the transition with even greater precision, providing that the recognition of the colour-change is not more difficult. The quantity of indicator employed must be so small that the amount of alkali required to neutralise it is negligible.

For Theory of Indicators, *v.* Ostwald (Scientific Foundations of Analytical Chemistry, translated by McGowan), Küster (Zeitsch. anorg. Chem. 1897, 13, 127), Waddell (J. Phys. Chem. 1898, 2, 171), Vaillant (Compt. rend. 1903, 136, 1192), Stieglitz (J. Amer. Chem. Soc. 1903, 25, 1112; Amer. Chem. J. 1908, 39, 651; 1909, 42, 115), McKoy (Amer. Chem. J. 1904, 31, 503), Hewitt (Analyst, 1908, 33, 85), Salm (Zeitsch. physical. Chem. 1906, 57, 471; Zeitsch. Elek. Chem. 1907, 13, 125), Salessky (Zeitsch. Elek. Chem. 1904, 10, 204), Fels (Zeitsch. Elek. Chem. 1904, 10, 208), Schoorl (Chem. Zentr. 1907, i 300, 502, 585), Hantzsch (Ber. 1907, 40, 1556; 1908, 41, 1187; 1915, 48, 158), Rohland (Ber. 1907, 40, 2172), Acree (Amer. Chem. J. 1908, 39, 528, 649, 789), Handa (Ber. 1909, 42, 3179); and *cf.* Noyes for the physico-chemical theory (J. Amer. Chem. Soc. 1910, 32, 815), Wegscheider (Zeitsch. physikal. Chem. 1915, 90, 641).

Indicators may be divided broadly into three classes: (i.) Those insensitive to very weak acids, such as carbonic, boric, and hydrosulphuric acids; these indicators comprise among others *methyl orange*, *lacmoid*, *cochineal*, and *iodoeosin.* (ii.) Those somewhat sensitive to weak acids, although as a rule these acids cannot be accurately titrated with their aid; if weak volatile acids such as carbonic acid are removed by boiling, these indicators act like those of the first class towards fairly strong acids and bases. *Litmus* is the chief representative of this group. (iii.) Those highly sensitive even to weak acids. This class contains *phenolphthalein*, *turmeric*, and *rosolic acid* (*v.* Glaser, Zeitsch. anal. Chem. 1899, 38, 273; Wagner, Zeitsch. anorg. Chem. 1901, 27, 238).

The more important indicators are described below in alphabetical order.

Aurin (*Commercial or para-Rosolic acid*) is a mixture of several substances, produced by heating together phenol and oxalic and sulphuric acids; it appears in commerce in yellowish-brown resinous lumps. A 1 p.c. solution in 60 p.c. alcohol is employed, 1·5 c.c. being added to the solution to be titrated. In acid solution the colour is pale *yellow*, in alkaline solution *rose-red*. This indicator is very sensitive and well adapted for titrating barium hydroxide solutions, but it is affected by carbon dioxide and hydrogen sulphide.

Cochineal. The colouring matter in the product obtained from the dried female insect *Coccus cacti* (Linn.), is termed *carminic acid*. The best trade product, which is called 'silver cochineal,' was first recommended as an indicator by Luckow (J. pr. Chem. 1861, 84, 424; Zeitsch. anal. Chem. 1862, 1, 386); 3 grams of the substance (not pulverised) is extracted with 250 c.c. of dilute alcohol (1 vol. alcohol : 3–4 vols. water), and the clear liquid decanted. In alkaline solution the colour is *violet*, in acid *yellowish-red*. This indicator, which is very sensitive to strong acids and bases, is extremely useful in titrating ammonia; it is scarcely affected by carbon dioxide. The colour-change is well defined even in artificial light. Cochineal is, however, useless for titrating organic acids; and iron, aluminium and copper salts must be absent, since their solutions remain pink even when acid.

Curcumin (*Turmeric yellow*). The colouring matter from the roots of *Curcuma longa* (Linn.) is turned *yellow* by acids and *reddish-brown* by alkalis; it is nearly always employed as a *test-paper*, and is useful in detecting ammonia and boric acid.

Gallein (*Alizarin violet, Pyrogallolphthalein*). This compound, prepared by heating together pyrogallol and phthalic anhydride (Baeyer, Ber. 1871, 4, 457, 555, 663), was proposed as an indicator by Dechan (Pharm. J. 15, 849). A 0·1 p.c. alcoholic solution is used, 10 drops being added to 100 c.c. of liquid. In alkaline solution the colour is *reddish-violet*, in acid *pale-brown*. This indicator is scarcely affected by carbon dioxide, and can be used in the accurate titration of organic acids.

Iodoeosin (*Tetraiodofluorescein, Erythrosin B.*). This substance, prepared by iodating fluorescein, is a brick-red powder soluble in hot alcohol or in ether, but almost insoluble in water or cold alcohol; it was first recommended by Mylius and Forster (Ber. 1891, 24, 1482); 0·5 gram of the sodium derivative of iodoeosin is dissolved in 1 litre of water, 2·5 c.c. are added to the solution to be titrated together with 5 c.c. of chloroform, the mixture being shaken in a stoppered bottle during titration. While alkaline the aqueous layer is *rose red*, when acid the aqueous layer becomes *colourless*, and the chloroform assumes a yellowish tint (Ellms, J. Amer. Chem. Soc. 1899, 21, 359; M. and F. used ether instead of chloroform). With this indicator, centinormal or even millinormal solutions can be titrated; it is indifferent to carbon dioxide, and phosphoric acid can be titrated as a monobasic acid with sodium hydroxide (Glücksmann, Chem. Zentr. 1902, (i.) 1131). Feeble bases, such as the alkaloids, may also be titrated, using iodoeosin as indicator.

Lacmoid (*Resorcin Blue*). This substance is obtained by heating gradually to 110° a mixture of 100 parts of resorcinol, 5 parts of sodium nitrite, and 5 parts of water. When the violent reaction moderates, the mass is heated to 115°–120° until evolution of ammonia ceases. The product is a glistening reddish powder (Traub and Hock, Ber. 1884, 17, 2615). It owes its distinctive properties to *lacmosol*, which can be isolated and purified by a method described by Hottinger (Biochem. Zeitsch. 1914, 65, 177). The turning-point of the pure indicator is far sharper than that of the ordinary preparation.

A 0·3 p.c. alcoholic solution is employed; a better colour change is produced if 5 grams of naphthol green are dissolved in a litre of this solution (Zeitsch. angew. Chem. 1890, 3, 163). In alkaline solution the colour is *blue*; in acid, *red*. Although these colour changes resemble those of litmus, the indicator is more closely allied to methyl orange. It is only slightly affected by carbon dioxide, although direct titration of carbonates is not satisfactory in cold solution; lacmoid test paper may, however, be used in almost any experiment for which methyl orange is suitable. This indicator is useless for organic acids.

Litmus occurs in commerce in the form of small cubical granules mixed with a large proportion of calcium carbonate. An aqueous solution of this product not only contains free alkali, but also a variable proportion of colouring matters which interfere with the delicacy of the reaction. Special precautions must therefore be taken in preparing the solution for use in acidimetry. Various processes have been recommended by Berthelot and De Fleurieu (Ann. Chim. Phys. 1865, [4] 5, 189), Wartha (Ber. 1876, 9, 217), Mohr (Titrirmethode), Luttke (Zeitsch. anal. Chem. 1892, 31, 692). The following method gives excellent results: The litmus is extracted three or four times with boiling methylated alcohol of 85 p.c. in order to remove the injurious colouring matters, the residue is extracted with cold water, slightly acidified with sulphuric acid, and boiled to expel carbon dioxide. The extract is neutralised with baryta water, a few bubbles of carbon dioxide passed in to remove excess of baryta, and the liquid again boiled and filtered. The solution should contain about 20 grams of solid matter per litre, and must be kept in vessels to which the air has free access. If kept in closed vessels it undergoes fermentation and is decolourised. The colour is restored when the liquid is exposed to air. The colour of the solution should be *purple*; it turns *blue* with alkalis, and *red* with acids, and is affected by carbon dioxide, sulphur dioxide, and hydrogen sulphide. (For the relative merits of litmus and methyl orange, *v.* Reinitzer, Zeitsch. angew. Chem. 1894, 547, 574; Lunge, *ibid.* 1894, 733.)

The colour change is rendered more delicate by conducting the titration in the monochromatic light obtained by heating a bead of sodium carbonate in a bunsen flame (L. Henry, Compt. rend. 1873, 76, 222). The red solution seems colourless, whilst the blue solution is almost black. Litmus is not well adapted for use by gas- or lamp-light.

Luteol. The preparation of this substance, a hydroxychlorodiphenylquinoxaline, is described by Autenrieth (Arch. Pharm. 1895, 233, 43), and by Glaess and Bernard (Mon. Sci. 1900, 14, 809); it forms fine, woolly, yellowish needles, m.p. 246°. A 0·33 p.c. alcoholic solution is used as an indicator. In alkaline solution the colour is *yellow*; in acid it is *colourless*. This indicator is said to be remarkably sensitive, excelling Nessler's solution as a test for ammonia; but it is sensitive to carbon dioxide (Higgins, J. Soc. Chem. Ind. 1900, 19, 958). It was especially recommended by Autenrieth for use in Kjehldahl's process (*v.* ANALYSIS).

Methyl orange (*Helianthin, Poirrier's Orange III*). This substance, prepared by diazotising sulphanilic acid and coupling the resulting diazonium salt with dimethylaniline, was introduced as an indicator by Lunge (Ber. 1878, 11, 1944; J. Soc. Chem. Ind. 1882, 1, 16). One gram of pure methyl orange (either the free acid or its sodium salt) is dissolved in 1 litre of water, and two drops of this solution are added in each titration; if, owing to dilution during the titration, the colour becomes too faint, another drop of the indicator is added; on no account should too much indicator be used, since the colour change, from *yellow* in alkaline to *pink* in acid solution, is not sharp in such circumstances. Methyl orange is exceedingly useful, since its indications are practically unaffected by the presence of carbonic, hydrosulphuric, boric, and silicic acids; carbonates and sulphides may therefore be titrated in cold solution as if they were hydroxides. All titrations must be made with this indicator in cold aqueous solution, and, since methyl orange is not very sensitive as compared with various other indicators, the acid or alkali employed should be fairly concentrated. It is advisable to employ normal solutions, though with N/2 or even N/5 solutions it is possible to determine an end-point to within a single drop. With N/10 solutions, especially when carbonates are being titrated, there is a distinct *brownish* transition tint between the yellow and pink, and results may be uncertain to the extent of one or two drops (*cf.* Küster, Zeitsch. anorg. Chem. 1897, 13, 140).

The addition of indigo-carmine to methyl orange has been recommended by Luther (Chem. Zeit. 1907, 31, 1172), who states that the colour change is very pronounced. Ethyl orange is stated by Wieland to be even better than methyl orange (Ber. 1883, 16, 1989).

Methyl red. This substance, prepared by diazotising anthranilic acid and coupling the resulting diazonium salt with dimethylaniline, was introduced as an indicator by Rupp and Loose (Ber. 1908, 41, 3905). A 0·2 p.c. alcoholic solution is employed, and two drops of this are added in each titration. The colour change is from a pure *yellow* in alkaline to a *reddish-violet* in acid solution, and is very pronounced. This indicator is very sensitive, and can be used for titrating weak bases in centinormal solution. Ordinary sodium hydroxide solutions containing a little carbonate can be accurately titrated in the cold.

According to Thomson (Analyst, 1914, 39, 518) methyl red gives a sharper end point than methyl orange, and its sensitiveness, unlike that of methyl orange, is not greatly affected by the presence of neutral salts. When methyl red is used in the titration of carbonates, the solution must be boiled after each addition of the acid. *See* also Lehmann and Wolff, Arch. Pharm. 1917, 255, 113.

For observations on the behaviour of indicators of the methyl-red type, *see* Howard and Pope, Chem. Soc. Trans. 1911, 1333.

Phenacetolin, first recommended by Degener (Zeit. d. Ver. f. d. Rübenzucker Industrie, 1881, 357; J. Soc. Chem. Ind. 1882, 1, 85), is prepared by boiling together for several hours molecular proportions of phenol, acetic anhydride, and sulphuric acid. The product is extracted with water to remove excess of acid, dried and dissolved in alcohol in the proportion of 1 gram to 500 c.c. It is *pale yellow* with alkalis, *red* with carbonates of the alkalis and alkaline earths, *colourless* or *pale yellow* with acids. It is used for estimating both hydroxide and carbonate when present in the same solution.

Phenolphthaleïn, obtained by heating phenol with phthalic anhydride and concentrated sulphuric acid (Baeyer, Annalen, 1880, 202, 69), was proposed as an indicator by Luck (Zeitsch. anal. Chem. 1877, 16, 322). One or two drops of a 0·5 p.c. alcoholic solution are used in each titration. In alkaline solution the colour is *red*; the acid solution is *colourless*. Owing to its very weak acid character, phenolphthaleïn is the indicator *par excellence* for organic acids; it is useless, however, in the presence of ammonium salts, and since even carbonic and hydrosulphuric acids discharge the red colour, it is necessary to work with solutions free from these acids or titrate in boiling solution; hence its use is somewhat restricted (*cf.* McBain, Chem. Soc. Trans. 1912, 101, 814). A convenient method of titrating organic acids with ordinary sodium hydroxide solutions using phenolphthaleïn as indicator, is described by Philip (Chem. Soc. Trans. 1905, 87, 991); *cf.* McCoy (Amer. Chem. J. 1904, 31, 503); and Schmatolla (Ber. 1902, 35, 3905).

Turmeric *v.* CURCUMIN.

Many other indicators have been proposed from time to time, among others the following:—

Alizarin (Schaal, Ber. 1873, 6, 1180); *Alizarin-red* I. W.S. (Knowles, J. Soc. Dyers, 1907, 23, 120); *Congo-red*; *cyanine* (Schönbein, J. pr. Chem. 1865, 95, 449); *cyanogen iodide* (Kastle and Clark, Amer. Chem. J. 1903, 30, 87); *diaminazoatoluenesulphonic acid* (Troeger and Hille, J. pr. Chem. 1903, 68, 297); *ferric salicylate* (Weiske, J. pr. Chem. 1875, 12, 157; Wolff, Compt. rend. 1900, 130, 1128; Gerock, Chem. Zentr. 1900, ii. 1294); *flavescin* (Lux, Zeitsch. anal. Chem. 1880, 19, 457); *fluorescein* (Krüger, Ber. 1876, 9, 1572; Zellner, Chem. Zeit. Rep. 1901, 25, 40); *hæmatoxylin* (Wildenstein, Zeitsch. anal. Chem. 1863, 2, 9); *metanil yellow* (Linder, J. Soc. Chem. Ind. 1908, 27, 485); *methyl*-3-*aminoquinoline* (Stark, Ber. 1907, 40, 3434); *extract of mimosa flowers* (Robin, Compt. rend. 1904, 138, 1046); *para-nitrophenol* (Langbeck, Chem. News, 1881, 43, 161; Spiegel, Ber. 1900, 33, 2640; Zeitsch. angew. Chem. 1904, 17, 715; Goldberg and Naumann, Zeitsch. angew. Chem. 1903, 16, 644); *paranitrobenzeneazo-α-naphthol* (Hewitt, Analyst, 1908, 33, 85); and *Poirrier's blue* C4B (Engel, Compt. rend. 1886, 102, 214); 2·5-*Dinitroquinol* (Henderson and Forbes, J. Amer. Chem. Soc. 1910, 32, 687); *di-o-hydroxystyryl ketone* (*lygosin*) (Ferenz); 1-*oxynaphtho-*

chinomethane (Nierenstein); 6-*sulpho-α-naphthol-*1-*azo-*m-*hydroxybenzoic acid* (Mellet); 2·6-*dinitro-aminophenol* (*isopicramic acid*) (Meldola and Hale); *alizarinmonosulphonic acid* (Knowles); *myrtle berry* (*Vaccinius myrtillus*, L.) juice, the colouring matter of which is œnocyanin, the red colouring matter of wine; *red beetroot extract* (Chauvierre).

The relative sensitiveness of the more important indicators and their behaviour under various conditions have been investigated by Wieland (Ber. 1883, 16, 1989), and especially by Thomson (Chem. News, 1883, 47, 123, 135, 184; 1884, 49, 32, 38, 119; 1885, 52, 18, 29), whose results are summarised in the following table:—

—	Litmus	Lacmoid	Aurin	Methyl orange	Phenacetolin	Phenolphthalein
Sensitiveness	0·05	0·01	0·01	0·05	0·01	0·01
Hot solutions	Available	Available	—	—	—	—
Ammonia	Available	Available	Available	Available	Available	Not available
Ammonium salts	Not affected	Not affected	Less sensitive	Less sensitive	Not affected	Not available
Neutral alkaline salts	Not affected	Not affected	Not affected	Less sensitive	Not affected	Not affected
Carbon dioxide	Indefinite	Indefinite	Indefinite	Not affected	Colour changed	Indefinite
Hydrogen sulphide	Indefinite	Decolourised	Indefinite	Not affected	Not affected	Indefinite
Alkaline carbonates	Indefinite	Indefinite	Indefinite	Alkaline	Red colour	Alkaline
Alkaline bicarbonates	Indefinite	Indefinite	Indefinite	Alkaline	—	Neutral
Sulphites	Indefinite	Alkaline	Neutral	Alkaline	Not available	Neutral
Acid sulphites	Indefinite	Neutral	Acid	Neutral	Not available	Acid
Silicic acid	Neutral	Neutral	Neutral	Neutral	Neutral	Not available
Alumina	Indefinite	Alkaline	Indefinite	Alkaline	Neutral	Neutral
Boric acid	Indefinite	Indefinite	Indefinite	Neutral	Indefinite	Indefinite
Sodium thiosulphate	Neutral	Neutral	Neutral	Neutral	Neutral	Neutral
Sulphides	Alkaline	Not available	—	Alkaline	Alkaline	Alkaline
Hydrosulphides	Indefinite	Not available	—	Alkaline	—	Neutral
Potassium nitrite	Neutral	—	Neutral	Destroyed	Neutral	Neutral
Oxalic acid	Available	Not available	Available	Not available	Not available	Available
Phosphoric acid	Indefinite	Monobasic	Indefinite	Monobasic	Indefinite	Dibasic
Arsenic acid	Indefinite	Monobasic	Indefinite	Monobasic	Monobasic	Dibasic
Arsenious acid	Neutral	Neutral	Indefinite	Neutral	Neutral	Indefinite
Phenol	Neutral	Neutral	Neutral	Neutral	Neutral	Indefinite

The sensitiveness is measured in c.c. of decinormal acid required to produce a distinct change when the volume of the liquid is 100 c.c. It should be borne in mind, however, that the sensitiveness of many indicators changes (usually diminishes) in the presence of considerable quantities of dissolved salts. Where a reaction is given as 'indefinite,' it is not meant that there is no effect, but that the change is not sufficiently sharp to be available in analysis. In many cases where the reaction is indefinite in cold solutions it becomes definite if the liquid is boiled, *e.g.* litmus with sulphides, sulphites, and carbonates; phenolphthalein with sulphides and carbonates. Lacmoid is most serviceable in the form of paper, and several of the reactions which are unsatisfactory with the solution are sharp and distinct with the paper, *e.g.* with carbonates, sulphides, and sulphites

Gawalowski recommends (Zeitsch. anal. Chem. 1883, 22, 397) the use of a mixture of methyl orange and phenolphthaleïn, which is deep-red with excess of alkali, pale-yellow when neutral, and rose-red with excess of acid. Compare also Schlotz (Zeitsch. Elek. Chem. 1904, 10, 549) on mixed indicators.

Walpole (Biochem. J. 1914, 8, 628) gives a chart of hydrogen ion concentration data representing the sensitive ranges of all the indicators in general use, both in colorimetric and 'end-point' processes.

Preparation of Standard Acids and Alkalis.

Standard solutions of acids and alkalis are usually prepared on the *normal* basis, the *normal* solution of a chemical reagent containing one gram-equivalent of the substance in one litre of the solution (*v.* ANALYSIS, Volumetric section).

In acidimetry and alkalimetry it is essential to have a standard solution of some acid or alkali, the concentration of which is known with great accuracy; this solution serves to standardise the others. Various suggestions have been made, but the general choice, at least for technical purposes, has fallen on hydrochloric acid as the standard acid; sulphuric acid is frequently employed and, less often, oxalic acid.

The commonest method of fixing the exact concentration of the hydrochloric (or sulphuric) acid consists in titrating the acid against weighed amounts of pure anhydrous sodium carbonate, a process originally employed by Gay-Lussac, and strongly recommended by Lunge, Sutton, and Treadwell. Separate weighed quantities of the pure carbonate are dissolved in 50–100 c.c. of cold distilled water, and each titrated with the acid, using methyl orange as indicator. The concentration of the acid solution is calculated from each result, and the mean of the concordant values adopted as correct. Chemically pure sodium carbonate is obtainable in commerce, and should be free from all but traces of chloride and sulphate; it is dried in a platinum crucible with continual stirring for 20–30 minutes at such a temperature that the crucible bottom is barely red hot, or the crucible, embedded in sand, may be heated at 300° for half an hour. Pure sodium carbonate may also be prepared by heating the bicarbonate at a temperature not exceeding 300° (Lunge, Zeitsch. angew. Chem. 1897, 10, 522). Sulphates and chlorides are removed from the bicarbonate by washing with cold water. (For the preparation of pure sodium bicarbonate, *v.* Reinitzer (Zeitsch. angew. Chem. 1894, 7, 551), and North and Blakey (J. Soc. Chem. Ind. 1905, 24, 396).)

The foregoing method, although extensively used, has been adversely criticised, the chief objection being that it is impossible to dehydrate the carbonate or bicarbonate without losing a little too much carbon dioxide. It is asserted that sodium oxide is present even when the temperature of drying has not exceeded 170°; *v.* Kissing (Zeitsch. angew. Chem. 1890, 3, 262);

Higgins (J. Soc. Chem. Ind. 1900, 19, 958); Sörensen and Andersen (Zeitsch. anal. Chem. 1905, 44, 156); North and Blakey (J. Soc. Chem. Ind. 1905, 24, 396); Sebelin (Chem. Zeit. 1905, 29, 638); but *cf.* Seyda (Chem. Zentr. 1899, (i.) 1164); Lunge (Zeitsch. anal. Chem. 1904, 17, 231; 1905, 18, 1520).

A satisfactory method of checking the values obtained by the carbonate method depends on the fact that sodium oxalate, when heated, is converted into sodium carbonate. As this oxalate can be prepared in a high degree of purity, the residue of carbonate theoretically obtainable from a known weight of oxalate can be calculated, and the presence of any sodium oxide is immaterial providing that all calculations are based on the original weight of sodium oxalate.

The weighed oxalate is carefully heated in a platinum crucible until all the separated carbon has been burnt off and the residual carbonate begins to fuse; the cooled residue is dissolved in water and titrated as already described; *v.* Sörensen (Zeitsch. anal. Chem. 1897, 36, 639; 1903, 42, 333, 512; 1905, 44, 156), Lunge (Zeitsch. angew. Chem. 1905, 18, 1520); and ANALYSIS, (Volumetric section, standardisation of permanganate).

From time to time many other standards have been proposed, and among others the following:—

Potassium tetroxalate; succinic acid (Phelps and Hubbard, Zeitsch. anorg. Chem. 1907, 53, 361; Phelps and Weed, *ibid.* 1908, 59, 114, 120); *borax* (Rimbach, Ber. 1893, 26, 171); *potassium hydrogen tartrate* (Borntrager, Zeitsch. anal. Chem. 1892, 31, 43); *potassium dichromate* (Richter, Zeitsch. anal. Chem. 1882, 21, 205); *potassium iodate* (Fessel, Zeitsch. anal. Chem. 1899, 38, 449); *potassium biiodate* (Meineke, Chem. Zeit. 1895, 19, 2); *sodium* (Hartley, Chem. Soc. Trans. 1873, 26, 123; Neitzel, Zeitsch. anal. Chem. 1893, 32, 422; *cf.* Hopkins, J. Amer. Chem. Soc. 1901, 23, 727); and *sulphuric acid*, prepared by electrolysing copper sulphate solution (Hart and Croasdale, Chem. News, 1891, 63, 93; Kohn, J. Soc. Chem. Ind. 1900, 19, 962).

Hydrochloric acid. In preparing a normal solution advantage may be taken of the fact that an aqueous solution of hydrogen chloride which boils at a constant temperature has a practically constant composition. A quantity of ordinary concentrated acid is distilled from a capacious retort until one-third has passed over. The residual liquid will contain 20·2 p.c. of hydrogen chloride, and 165 c.c. when diluted to 1 litre will form an almost exactly normal solution; it should be standardised by one of the following processes.

The strong acid is diluted until its specific gravity is approximately 1·1, and distilled; after three-fourths of liquid have passed over, the remaining distillate is collected apart, and the barometric height observed. The final quarter of the distillate is of perfectly definite composition, and the following table gives the actual content of hydrogen chloride for a definite barometric height, together with the weight of distillate which contains one gram-equivalent of hydrogen chloride, *i.e.* which yields a normal solution when diluted to 1 litre:—

Barometer	%HCl	Grams of mixture containing 1 mol. HCl
770	20·218	180·390
760	20·242	180·170
750	20·266	179·960
740	20·290	179·745
730	20·314	179·530

These results were calculated from the observed weights of liquid, without reduction to vacuum standard; the compositions were determined gravimetrically by precipitation as silver chloride (Hulett and Bonner, J. Amer. Chem. Soc. 1909, 31, 390).

The simplest method of preparing a large quantity of nearly normal hydrochloric acid is to find the approximate composition of the ordinary concentrated acid by taking its specific gravity with a hydrometer and referring to a suitable table; the requisite quantity of the acid is then measured out and appropriately diluted with distilled water.

To standardise the solution, it is titrated against successive weighed quantities of pure sodium carbonate (or sodium oxalate), as described above. Each separate amount of carbonate should weigh from 2·0 to 2·5 grams in order to ensure a burette reading of 40 to 50 c.c. It is best to use methyl orange for indicator, since the titrations can be rapidly and accurately carried out in the cold; if litmus is used, the titration must be made in boiling solution. In the latter case, it is quicker to add a measured excess of acid to the carbonate, and titrate back with sodium hydroxide the value of which is known in terms of the acid; but the titration must nevertheless be done in boiling solution. The calculation is very simple: if x grams of sodium carbonate require y c.c. of hydrochloric acid, then 1 c.c. acid $= x/y$ grams of sodium carbonate. Now, 1 c.c. N-acid $=0{\cdot}05300$ grams sodium carbonate, and hence

$$\text{concentration of acid} = \frac{x}{0{\cdot}053y} \text{ times normal}$$

$=z$ times normal, say. As a rule, this is a very convenient method of expressing the result; *e.g.* if the acid is used to estimate an alkali of equivalent e, then 1 c.c. acid $= \frac{e}{1000} \times z$ grams of alkali. If necessary, the acid solution may be diluted with distilled water so that the ratio final volume ÷ initial volume $= z$; it will then be exactly normal. A simple arithmetical calculation is required, and if this process is contemplated, care should be taken initially to ensure that z shall be slightly greater than unity.

Hydrochloric acid is most accurately standardised gravimetrically by precipitating chlorine with excess of silver nitrate and weighing the silver chloride in a Gooch crucible. The solution may be titrated against pure silver according to the Mint process for assaying this metal. The method may be modified by adding the silver solution in very slight excess, this excess being determined in the filtrate with N/10-thiocyanate (Thorpe's Quantitative Analysis; Dittmar's Quantitative Analysis; Knorr, J. Amer. Chem. Soc. 1897, 19, 814; Hopkins, *ibid.* 1901, 23, 727). These methods are trustworthy only when the hydrochloric acid is free from chlorides.

The following method depending on the loss of weight on converting silver nitrate into chloride is due to Andrews (J. Amer. Chem. Soc.

1914, 36, 2089). Two similar silica dishes are provided with watch-glass covers, and one of them with a stirring-rod, short enough to lie under the cover. Into this dish about 2 grams silver nitrate are put, and both dishes are placed in an oven at 160°, the temperature being subsequently raised to 244°. After cooling in a desiccator, both dishes are weighed. Fifty c.c. of $\frac{N}{5}$ hydrochloric acid to be standardised are run into each dish, the contents of which are then evaporated on the water-bath, and finally dried at 240°. The normality of the solution is given by the expression:

$$N=\frac{W-W_1+w_1-w}{0{\cdot}02656V}$$

in which V = volume of acid delivered by the 50 c.c. pipette; W = weight in air of silver nitrate and dish, W_1 = weight of dish with mixed chloride and nitrate, w = weight of control-dish before, and w_1 its weight after experiment (Analyst, 1815, 24).

A simple and accurate process of standardisation consists in immersing weighed pieces of Iceland spar in a measured volume of the acid, and noting the loss in weight of the spar after the acid is neutralised (Masson, Chem. News, 1900, 81, 73; Green, *ibid.* 1903, 87, 5; *cf.* Thiele and Richter, Zeitsch. angew. Chem. 1900, 13, 486).

Small quantities of standard hydrochloric acid may be prepared by absorbing dry hydrogen chloride in a weighed quantity of water and ascertaining the increase in weight (Moody, Chem. Soc. Trans. 1898, 73, 658; Higgins, J. Soc. Chem. Ind. 1900, 19, 958; Acree and Brunel, Amer. Chem. J. 1906, 36, 117).

Sulphuric acid. An approximately normal solution is obtained by diluting to 1 litre 28 c.c. of pure concentrated sulphuric acid (sp.gr. 1·84). The solution may be standardised with pure sodium carbonate or oxalate (*v.* HYDROCHLORIC ACID), or a measured quantity treated with a slight excess of ammonia, evaporated to dryness, and the residual ammonium sulphate heated at 120° and weighed. This method gives trustworthy results only when pure redistilled acid is employed in preparing the solution (Weinig, Zeitsch. angew. Chem. 1892, 5, 204; Shiver, J. Amer. Chem. Soc. 1895, 17, 351; Hopkins, *ibid.* 1901, 23, 727; Marboutin and Pécoul, Bull. Soc. chim. 1897, 17, 880).

A measured volume of the acid is added to a weighed excess of sodium carbonate in a platinum dish, the solution evaporated, the residue dried at 300° and weighed. The change in weight due to the transformation of sodium carbonate into sulphate indicates the amount of acid present in the solution. This method is much preferable to precipitating and weighing the acid as barium sulphate (Thorpe, Quantitative Analysis, 1873. (*Cf.* Richardson, J. Soc. Chem. Ind. 1907, 26, 78.)

Sulphuric acid solutions of definite concentration may be prepared by specific gravity measurements (Pickering, Chem. Soc. Trans. 1890, 57, 64). A quantity of the purest acid is diluted with half its volume of water, and the specific gravity of the mixture accurately determined at 15° or 18° in a Sprengel pyknometer. The percentage of sulphuric acid in the solution is then obtained by reference to tables giving the values for 15°/15° or 18°/18° (*v.* Sutton's Volumetric Analysis, 9th ed., or J. Soc. Chem. Ind. 1899, 18, 4). The table given in J. Soc. Chem. Ind. 1902, 21, 1511, may be employed when the specific gravity (15°/15°) has been calculated without introducing any vacuum corrections, which must be allowed for if the other tables are employed. Between the limits of 66 p.c. and 81 p.c. the following formulæ reproduce the values in the tables with an error not exceeding 0·04 p.c.:—

$$P=86\,S_{15}-69{\cdot}00$$
$$P=86\,S_{18}-68{\cdot}82$$

where P = percentage of sulphuric acid, and S_{15} and S_{18} = the specific gravities referred to water at 15° and 18° respectively, calculated without allowing for 'air displaced' (Marshall, J. Soc. Chem. Ind. 1899, 18, 4). The diluted acid may be kept in a stoppered bottle without change, and by weighing out the appropriate amount and diluting to a litre, a normal solution of sulphuric acid can be rapidly prepared.

Oxalic acid. A normal solution is prepared by dissolving 63·02 grams of the recrystallised hydrated acid $H_2C_2O_4+2H_2O$ in water and diluting to 1000 c.c. As the crystallised acid is somewhat efflorescent, especially on slightly warming, it may contain less than two molecular proportions of water. The solution may be checked against a standard alkali, using phenolphthaleïn as indicator, or against an accurately standardised permanganate solution (*cf.* Treadwell-Hall, Analytical Chemistry, vol. 2).

Oxalic acid solutions do not keep very well. A small quantity of metallic mercury added to the solution tends to stabilise it.

Sodium hydroxide. To prepare a normal solution, clear transparent lumps of the best white commercial caustic soda are selected, any opaque portions of their surface scraped off, and 50 grams of the substance weighed out for each litre of solution. The cooled solution is standardised against the standard hydrochloric acid, using methyl orange as indicator, and taking 50 c.c. for each titration.

For the preparation of sodium hydroxide solutions free from carbonate, *v.* Küster (Zeitsch. anorg. Chem. 1897, 13, 134; 1904, 41, 472, and Bousfield and Lowry, Phil. Trans. 1905, 204, 253).

Potassium hydroxide *cf.* SODIUM HYDROXIDE.

Barium hydroxide. An approximately N/10-solution is best prepared from the crystalline hydroxide $Ba(OH)_2, 6H_2O$. The powdered substance is shaken with distilled water, the solution allowed to settle, the clear liquid siphoned off and diluted with an equal volume of recently boiled-out water. The solution must be kept permanently in contact with that portion already in the burette, and guard tubes are required to prevent access of carbon dioxide. The solution is standardised against succinic acid, phenolphthaleïn being used as indicator; or a measured volume may be evaporated to dryness with a slight excess of pure sulphuric acid, the residual barium sulphate being gently heated and weighed.

The chief use of this solution is in titrating organic acids, using phenolphthaleïn as indicator. For this purpose carbon dioxide must be excluded, and barium hydroxide is consequently the most convenient alkali to employ.

Ammonia. This solution is not often employed; an approximately semi-normal solution, readily obtained by diluting 28 c.c. of concentrated ammonia solution to 1 litre, is titrated against hydrochloric acid in the cold, using methyl orange as indicator; phenolphthaleïn cannot be employed.

Schultze has determined the rates of expansion of normal solutions of acids, and alkalis and other solutions employed in volumetric analysis (Zeitsch. anal. Chem. 1882, 21, 170). The following are the results for average temperatures:—

—	Oxalic acid	Hydrochloric acid	Nitric acid
0°	10000	10000	10000
10°	10010	10010	10018
15°	10019	10019	10031
20°	10031	10030	10045
25°	10046	10043	10061

—	Sulphuric acid	Potassium hydroxide	Sodium hydroxide
0°	10000	10000	10000
10°	10017	10019	10021
15°	10029	10031	10034
20°	10044	10046	10048
25°	10060	10062	10065

TYPICAL ACIDIMETRIC AND ALKALIMETRIC ESTIMATIONS.

Determination of total alkali. A weighed quantity of the substance (10 grams) is dissolved in water, filtered if necessary, and diluted to 500 c.c.; 50 c.c. are withdrawn, mixed with a measured excess (25 c.c.) of normal acid, boiled gently for ten minutes to expel carbon dioxide, and the excess of acid determined with standard alkali. The volume of standard acid *minus* the excess of acid gives the volume of acid required to neutralise the total alkali, *i.e.* the alkali present as hydroxide, carbonate, sulphide, sulphite, thiosulphate, aluminate, and silicate. If methyl orange is used as indicator, boiling is unnecessary, and the alkaline solution is titrated directly with standard acid. If direct titration with litmus as indicator is preferred, the solution must be continuously boiled during the titration.

Alkaline hydroxide in presence of carbonate. 100 c.c. of the above solution are heated, mixed with excess of barium chloride, allowed to cool, diluted to 250 c.c. and well shaken. When the precipitate has settled, 50 c.c. of the clear liquid are withdrawn and titrated with standard acid. The quantity of acid used × 25 gives the volume equivalent to the hydroxide in the weight of substance originally taken. The reaction which takes place is expressed by the equation

$$x\mathrm{M_2CO_3} + y\mathrm{MOH} + (x + \frac{y}{2})\mathrm{BaCl_2}$$

$$= x\mathrm{BaCO_3} + \frac{y}{2}\mathrm{BaH_2O_2} + (2x + y)\mathrm{MCl}.$$

The barium carbonate is precipitated and a quantity of barium hydroxide equivalent to the alkaline hydroxide remains in solution. The solution cannot be filtered, since the barium hydroxide would absorb carbon dioxide from the air with formation of the insoluble carbonate.

In order to avoid error due to the presence of the precipitate, and to economise time, Watson Smith (J. Soc. Chem. Ind. 1882, 1, 85) prefers to add just sufficient barium chloride to precipitate the carbonate without affecting the hydroxide. No barium remains in solution, and even if carbon dioxide is absorbed the alkaline carbonate formed remains in solution. The barium chloride is added gradually to the hot solution until precipitation is just complete, and the liquid is filtered into a 250 c.c. flask and an aliquot portion titrated. It is preferable for the liquid containing the precipitate to be diluted to 250 c.c., the precipitate allowed to settle, and 50 c.c. of the supernatant liquid withdrawn. (For various details and precautions, *v.* Sörensen and Andersen, Zeitsch. anal. Chem. 1908, 47, 279.)

Carbonate in presence of hydroxide. The solution is coloured a very faint yellow with phenacetolin, and standard acid is added until the yellow colour changes to a rose tint. The volume of acid required gives the amount of hydroxide present. A further quantity of acid is now added, and the red colour increases in intensity, but eventually changes to yellowish-red, and finally to golden-yellow. At this point a second reading is taken, and the difference between this and the first reading gives the volume of acid corresponding with the carbonate present (Lunge, J. Soc. Chem. Ind. 1882, 1, 56). This method is not available for the estimation of small quantities of hydroxide in presence of large quantities of carbonate (Thomson).

The following method, due to Warder, gives fairly satisfactory results: To the cold dilute solution phenolphthaleïn is added and standard hydrochloric acid run in slowly, the burette tip being immersed in the liquid, till decolourisation takes place. This occurs when all the hydroxide and *half* the carbonate have been neutralised. Methyl orange is then added and the solution titrated again till an acid reaction is indicated. If this second titration requires y c.c. and the first one x c.c., then the carbonate is equivalent to $2y$ c.c. and the hydroxide to $x - y$ c.c. (Küster, Zeitsch. anorg. Chem. 1896, 13, 127; Lunge, Zeitsch. angew. Chem. 1897, 10, 41; North and Lee, J. Soc. Chem. Ind. 1902, 21, 322; *cf.* Cameron, Amer. Chem. J. 1900, 23, 471).

In order to estimate the proportion of carbonate in quick-lime or slaked lime, the purpose for which phenacetolin was originally recommended by Degener, 100–150 grams of the lime are made into a cream with water and diluted to 500 c.c. After vigorous agitation 100 c.c. are withdrawn and diluted to 1000 c.c., and 25 c.c. of this liquid are taken, mixed with phenacetolin, and standard acid added until a pale-rose tint is obtained. In order to estimate both hydroxide and carbonate, the substance is dissolved in standard acid and the excess of acid determined by reverse titration in the usual way (Lunge, *l.c.*).

Acid carbonate in presence of normal carbonate. The *cold and dilute* solution of normal carbonate and acid carbonate is mixed with phenolphthaleïn, and standard acid added, the burette tip dipping into the liquid to prevent escape of carbon dioxide, until the liquid becomes colourless. At this point, which correponds with the complete conversion of the normal carbonate into acid carbonate, the volume of acid added is read off. The liquid is then boiled and acid is added gradually until the solution remains colourless even after long boiling, and the volume of acid is again read off. If x represents the first reading and y the econd reading, then $2x$ = the normal carbonate, and $y-2x$ = the acid carbonate (Warder, Chem. News, 1881, 43, 228).

Lunge (J. Soc. Chem. Ind. 1882, 1, 57) proposes a different method based on the reaction:

$$xM_2CO_3 + yMHCO_3 + zNH_3 + (x+y)BaCl_2$$
$$=(2x+y)MCl + yNH_4Cl + (x+y)BaCO_3 + (z-y)NH_3.$$

The solution to be tested is mixed with a meaured excess of standard (half-normal) ammonia, excess of barium chloride added, and the liquid diluted with recently boiled water to a definite volume. When the precipitate has settled, an aliquot portion of the clear liquid is withdrawn and titrated with standard acid in order to ascertain the excess of ammonia. The difference between the volume of ammonia added and that remaining after precipitation gives the volume corresponding with the quantity of acid carbonate n the liquid analysed.

By adding a definite excess of pure sodium hydroxide free from carbon dioxide, a mixture of normal carbonate and hydroxide is obtained which may be analysed as described above.

Ammonia. In order to determine the quanity of free ammonia in a solution of the gas, an accurately measured quantity (10 c.c.) of the iquid is transferred to a light tared flask, and weighed. This gives at once the weight taken or analysis and the sp.gr. The liquid is then titrated with standard acid in the usual way, using litmus, lacmoid, or methyl orange as ndicator.

Ammonia in combination is determined by boiling the substance with sodium hydroxide, eading the ammonia into a measured excess of tandard acid, and determining the residual acid with standard alkali. The substance is weighed nto a flask fitted with a cork, through one hole n which passes a pipette containing a strong solution of sodium hydroxide, whilst through another passes a tube leading to a flask or bulb U-tube containing a known volume of standard acid. The flask or U-tube is fitted with a cork which carries a calcium chloride tube containing beads moistened with some of the acid in order o ensure complete absorption of the ammonia. After addition of the sodium hydroxide solution the liquid is gently boiled for half an hour, and he residual acid determined. From the volume of acid which has combined with the ammonia the quantity of the latter is readily calculated. The sodium hydroxide may be replaced by milk of lime, and the most effectual method of removing the ammonia is to distil the mixture n steam. The use of magnesia in place of sodium hydroxide is not advantageous (Kober, J. Amer. Chem. Soc. 1908, 30, 1279). (For a different method of distilling off the ammonia, v. Kober (J. Amer. Chem. Soc. 1908, 30, 1131). *See* also Ronchèse (J. Pharm. Chim. 1907, 25, 11) and Wilkie (J. Soc. Chem. Ind. 1910, 29, 6) or a method of estimation entirely different in principle from the foregoing.)

Hydrochloric, Hydrobromic, Hydriodic, Sulphuric, and **Nitric acids** are readily estimated by direct titration with standard alkali, using methyl orange as indicator.

Oxalic, Tartaric, Citric, Acetic, and **Lactic acids** can likewise be titrated accurately with standard alkali if phenolphthaleïn is used as the indicator (Thomson, *l.c.*). Oxalic acid may also be titrated using litmus as indicator.

Boric acid gives no very definite reaction with the majority of indicators, but it is quite neutral to methyl orange, and hence the quantity of alkali in akaline borates can be accurately estimated by direct titration with standard acid if methyl orange is used as indicator (Thomson).

The titration of boric acid itself becomes possible if the solution contains at least 30 p.c. of its volume of glycerol. The boric acid then behaves towards phenolphthaleïn as a monobasic acid (Thomson, J. Soc. Chem. Ind. 1893, 12, 432; Jorgensen, Zeitsch. angew. Chem. 1897, 10, 5; Hönig and Spitz, *ibid.* 1896, 9, 549; Copaux, Compt. rend. 1898, 127, 756). A similar result is effected by saturating the solution with mannitol. Since phenolphthaleïn is employed, carbon dioxide must not be present in the solutions to be titrated (Jones, Amer. J. Sci. 1898, 7, 147; Stock, Compt. rend. 1900, 130, 516).

Sulphurous acid can be titrated directly if methyl orange, phenolphthaleïn, or aurin is used as indicator (Lunge, Dingl. poly. J. 250, 530). With methyl orange the hydrogen sulphite $MHSO_3$ is the neutral salt, whilst with the other two indicators the normal salt is neutral. This difference can be utilised for the determination of the relative proportions of normal and acid sulphite in the same solution (Blarez, Compt. rend. 1886, 103, 69; Chem. Soc. Abst. 1886, 50, 918). Caustic soda or potash must be used, since ammonia gives inaccurate results.

Phosphoric and **Arsenic acids** are monobasic with methyl orange, and dibasic with phenolphthaleïn (Joly, Compt. rend. 1882, 94, 529; Chem. Soc. Abst. 1882, 42, 692). These acids can be most accurately titrated with barium hydroxide, using phenolphthaleïn as indicator. Towards the close of the reaction, time must be allowed for the gelatinous tribarium phosphate to change into the crystalline dibarium salt (Joly, Compt. rend. 1886, 102, 316; Chem. Soc. Abst 1886, 50, 418). Advantage can be taken of the different basicity with methyl orange and phenolphthaleïn to estimate phosphoric acid in presence of monobasic acids such as hydrochloric acid (Joly, Compt. rend. 1885, 100, 55; Chem. Soc. Abst. 1885, 48, 348).

(For another simple and accurate method, *v.* Segalle, Zeitsch. anal. Chem. 1895, 34, 33.)

Carbonic acid in solution is estimated by adding excess of ammonia and calcium chloride. The liquid is then boiled, and the precipitated calcium carbonate collected, well washed, and dissolved in a measured excess of standard hydrochloric acid, the excess of acid being determined by means of standard alkali. The volume of normal acid actually used multiplied by 0·022 gives the quantity of carbon dioxide.

Insoluble carbonates are weighed into a flask fitted with a cork which carries a bulb and delivery tube. The bulb contains moderately strong hydrochloric acid, which is allowed to drop slowly on the carbonate, and the evolved gas is led into a flask containing strong ammonia solution. This flask is closed with a cork, through which passes the delivery tube, which ends just above the surface of the liquid. The cork also carries an exit tube filled with glass beads moistened with ammonia to arrest the last traces of carbon dioxide. When all the gas has been expelled from the carbonate the ammonia is mixed with calcium chloride, boiled, and the precipitate treated as above; *cf.* Gooch and Phelps (Amer. J. Sci. 1895, 50, 101). With slight modification this process can be adapted to the estimation of carbon dioxide in aërated waters.

For the direct titration of carbon dioxide in solution, *v.* Seyler (Analyst, 1897, 22, 312); Ellms and Beneker (J. Amer. Chem. Soc. 1901, 23, 405); and Forbes and Pratt (J. Amer. Chem. Soc. 1903, 25, 742).

Hydrofluoric acid may be accurately titrated with sodium hydroxide free from carbonate, using phenolphthaleïn as indicator (Winkler, Zeitsch. angew. Chem. 1902, 15, 33; *cf.* Haga and Osaka, Chem. Soc. Trans. 1895, 67, 251; and J. Amer. Chem. Soc. 1896, 18, 415; Monatsh. 1897, 18, 749).

Hydrofluosilicic acid may be titrated with sodium or barium hydroxide in the presence of alcohol (an equal volume is added) using phenolphthaleïn or lacmoid as indicator; the alcohol renders the salt produced insoluble in the solution; *v.* Sahlbom and Hinrichsen (Ber. 1906, 39, 2609); *cf.* Schucht and Moller (Ber. 1906, 39, 3693); and Honig and Szabadka (Chem. Zeit. 1907, 31, 1207).

Combined acids in salts may be estimated with approximate accuracy by adding to a solution of the salt a measured excess of sodium hydroxide or carbonate. The liquid is boiled, allowed to cool, and diluted to a definite volume. When the precipitate has settled, an aliquot portion of the clear liquid is withdrawn, and the excess of alkali determined by titration. From the volume of alkali used the proportion of acid in the salt is calculated. In order to avoid the error due to the presence of the precipitate, the liquid may be filtered before diluting to a definite volume, but methyl orange or cochineal must be used as indicator in order to avoid any error from carbon dioxide absorbed from the atmosphere. Salts of copper, silver, mercury, cobalt, nickel, iron, and chromium are precipitated with sodium hydroxide; salts of calcium, barium, strontium, magnesium, aluminium, zinc, bismuth, and manganese, with sodium carbonate.

Kieffer's method is useful for coloured solutions, or in presence of normal salts with acid reactions (Annalen, 1855, 93, 386). Sixty grams of crystallised cupric sulphate are dissolved in water, mixed with ammonia until the precipitate is almost but not quite dissolved, diluted to about 900 c.c., the solution left for some time, and the clear liquid siphoned off, or filtered through glass-wool, and diluted to 1000 c.c. If any further precipitate forms, it must be siphoned off or collected. If the solution of cuprammonium sulphate thus obtained is added to an acid liquid, so long as the acid is in excess an ammonium salt and cupric sulphate are formed, but as soon as the free acid is neutralised, the ammonia in a fresh quantity of cuprammonium sulphate reacts on the cupric sulphate already in the liquid and produces a precipitate of a basic salt, the formation of which indicates the point of saturation. The precipitate is most readily seen against a black background. In order to standardise the liquid, 10 c.c. of normal sulphuric acid are placed in a flask or beaker and Kieffer's solution added until a permanent precipitate is produced, and from the volume of solution required, its strength in terms of normal acid is readily calculated. The strength of the solution gradually diminishes, and it must be titrated from time to time. In making an actual determination, the Kieffer's solution is added to the liquid to be tested until a permanent precipitate is formed. The method is not very accurate owing mainly to the fact that the precipitate is not quite insoluble in solutions of ammonium salts, and therefore the end reaction does not take place until the liquid is saturated with the basic salt. The magnitude of the error depends on the concentration of the solution. When the liquids to be titrated contain barium, strontium, &c., the Kieffer's solution must be prepared with cupric nitrate.

(For other methods, *v.* Sims (Chem. News, 1907, 95, 253) and Ahlum (Chem. Soc. Proc. 1906, 22, 63).)

Bibliography.—Mohr's Chemisch-Analytische Titrirmethode, 6th ed. 1886; Sutton's Volumetric Analysis, 9th ed. 1904; Fresenius' Quantitative Chemische Analyse, v. 2, 6th ed.; Treadwell-Hall, Analytical Chemistry, v. 2, 2nd ed. 1910; Lunge's Technical Chemist's Handbook; Cohn's Indicators and Test Papers, 2nd ed. 1902; Glaser's Indikatoren der Acidimetrie und Alkalimetrie, 1901. G. T. M.

ACID ALIZARIN, -BLACK, -BROWNS, -PONCEAU, -YELLOWS *v.* AZO- COLOURING MATTERS.

ACID MAGENTA, ACID VIOLET *v.* TRIPHENYLMETHANE COLOURING MATTERS.

ACIDINE BRILLIANT RED *v.* AZO- COLOURING MATTERS.

ACIDOL. Trade name for betaine hydrochloride.

ACIERAL. An alloy, said to be made by first melting together Al 76, Ni 10, Ag 15, Co 2·5, Cu 3·5, W 0·5, Cd 1·0, Sn 1·5, in an electric furnace and stirring the fused mass into nine times its weight of aluminium, heated in a plumbago crucible lined with magnesia in an ordinary furnace (Fr. Pat. 473412, 1914). The alloy is silver-white, of sp.gr. 2·82, and m.p. 750°. Its tensile strength in castings is stated to be 30,000, in rods and sheets as 28,000–64,000, and heat-treated as 70,000 lbs. per square inch. It may be cast, forged, drawn, rolled, tempered, electroplated, and soldered. It is reported to have been used by the French Government for the manufacture of helmets (Eng. and Min. J. 1917, 103, 736).

ACITRIN. Trade name for the ethyl ester of 2-phenyl-quinoline 4-carboxylic acid. Used on account of its analgesic action in the treatment of sciatica and gout, and as uric acid eliminants.

ACME YELLOW *v.* AZO- COLOURING MATTERS.

ACOCANTHERA SCHIMPERI. The arrow-poisons of East Africa are prepared from the wood of the genus *Acocanthera*, which contains a crystalline glucoside, *acocantherinin* $C_{30}H_{46}O_{12}$, H_2O (Arnaud), $C_{32}H_{50}O_{12}$ (Faust). Crystallises from water and alcohol; insol. in ether or chloroform; sol. neutral and bitter. Strong sulphuric acid gives a red colour eventually becoming green. On boiling with dilute mineral acids is hydrolysed with formation of rhamnose. Is optically inactive, softens at 130° and decomposes at 220°. The pharmacological action of the glucoside resembles that of members of the digitalin group (Fraser and Tillie, Proc. Roy. Soc. 58, 70; Faust, Chem. Zentr. 1902, 2, [19] 1217; *cf.* STROPHANTHUS).

ACOINE. Trade name for *di-p*-anisylmonophenetylguanidine hydrochloride. Used as a local anæsthetic.

ACONITINE AND THE ACONITE ALKALOIDS. The alkaloids of the various species of *Aconitum* which have been examined chemically, fall into sharply differentiated groups. The first, of which aconitine itself is the type, includes a number of highly toxic alkaloids (*the aconitines*), which are diacyl esters of a series of polyhydroxy bases containing four methoxyl groups (*the aconines*). The following 'aconitines' are known :—

Aconitine from *Aconitum Napellus* (Linn.),
*Bikh*aconitine from *Aconitum spicatum* (Stapf.),
*Ind*aconitine from *Aconitum chasmanthum* (Stapf.),
*Jap*aconitine from Japanese aconite roots,
*Pseud*aconitine from *Aconitum deinorrhizum.*

The alkaloids of *A. Vulparia* (=*A. Lycoctonum*) and *A. septentrionale* constitute a second group of toxic alkaloids derived from aconites, while there is a third group which contains non-toxic alkaloids typified by atisine and comprises the following :—

Atisine from *Aconitum heterophyllum* (Wall.),
*Palm*atisine from *Aconitum palmatum* (D. Don.).

Aconitine is the principal alkaloid of *Aconitum Napellus* (Linn.), the common monkshood or wolfsbane (*Coqueluchon*, Fr.; *Eisenhut, Sturmhut*, Ger.), in which it occurs along with its decomposition products, benzaconine and aconine. *Aconiti radix,* B.P., is the full-grown daughter root only. *Aconitum,* U.S.P., is the root containing at least 0·5 p.c. of aconitine. *Aconitina*, B.P., U.S.P., is the alkaloid. Aconitine was isolated by Geiger and Hesse (Annalen, 1833, 7, 276), but first obtained in a crystalline state by Groves (Pharm. J. 1860, [ii.] 8, 121). Wright and Luff assigned to it the formula $C_{33}H_{43}O_{12}N$ (Chem. Soc. Trans. 1877, 31, 143; 1878, 33, 151, 318), and later Dunstan and his collaborators (*ibid.* 1891, 59, 271; 1892, 61, 385) adopted for it the formula $C_{33}H_{45}O_{12}N$, a slight modification of that used by Wright and Luff (*l.c.*). Until now almost all the work on crystallised aconitine had been done on alkaloid prepared from the roots of *Aconitum Napellus* grown in England. In 1894 analyses of the crystallised aconitine of commerce, probably from roots of *Aconitum Napellus* grown in Germany, were made by Freund and Beck, who assigned to the alkaloid the formula $C_{34}H_{47}O_{11}N$ (Ber. 1894, 27, 433), and their results were confirmed by Schulze (Arch. Pharm. 1906, 244, 167), who preferred the formula $C_{34}H_{44}O_{11}N$. This latter formula has been accepted by Dunstan and Henry (Trans. Chem. Soc. 1905, 87, 1650) as representing the composition of the present day aconitine of commerce. The earlier formulæ with less carbon are either due to botanical differences (the English root is now difficult to obtain) or to the escape of methane in the combustions.

Preparation. The finely-powdered root is exhausted with amyl alcohol mixed with three times its volume of wood spirit. From this extract the wood spirit is distilled under reduced pressure, leaving the whole of the alkaloids dissolved in the residue of amyl alcohol from which they are removed by agitation with dilute (1 p.c.) sulphuric acid. This acid aqueous liquid is shaken with ether to remove ether-soluble, non-basic substances, then made alkaline with dilute ammonia and the liberated alkaloids extracted with ether. The aconine remains dissolved in the water, the aconitine with some benzaconine passing into the ether. The ethereal solution is washed with a small quantity of water and evaporated. The residue is converted into hydrobromide by dissolving it in dilute hydrobromic acid, care being taken to avoid excess of acid. The exactly neutral liquid is evaporated to a small volume and allowed to crystallise. The aconitine hydrobromide is recrystallised until of constant melting-point, and then is converted into the alkaloid by the addition of a slight excess of ammonia to its aqueous solution, the alkaloid being extracted by ether in the usual way. The washed ethereal solution is dried by agitation with fused calcium chloride and evaporated. The small crystals, which are deposited as the ether evaporates, may be recrystallised from dry alcohol by the addition of ether.

Properties. Colourless, anhydrous hexagonal prisms, belonging to the rhombic system (Chem. Soc. Trans. 1891, 59, 288; Ber. 1894, 27, 722; Arch. Pharm. 1906, 244, 169). Easily soluble in chloroform or benzene, less readily in absolute alcohol or ether, very slightly soluble in water, almost insoluble in light petroleum. The aqueous solution is alkaline to litmus; m.p. 196°–197°. Dextrorotatory; in alcoholic solution $[\alpha]_D = +12° 32'$. Salts lævorotatory.

Aconitine is a most powerful poison (Cash and Dunstan, Phil. Trans. 1898, 190, 239). Between $\frac{1}{20}$ and $\frac{1}{50}$ of a grain has been recorded as a fatal human dose.

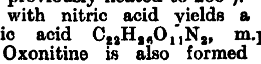
The ordinary salts of aconitine crystallise well. The hydrobromide $B{\cdot}HBr,2\frac{1}{2}H_2O$ is lævorotatory, $[\alpha]_D = -30{\cdot}47°$; m.p. 163° or 206° (anhydrous). The hydriodide, m.p. 226°, is crystalline, and sparingly soluble in water. The aurichloride $B{\cdot}HAuCl_4$ is thrown down as a pale-yellow amorphous precipitate from solutions of the hydrochloride and auric chloride. It crystallises from alcohol with $3H_2O$ and then melts at 135·5°; the anhydrous salt has m.p. 152° (Freund, Ber. 1894, 27, 724).

Reactions. When aconitine is heated at its melting-point it loses 1 mol. of acetic acid and furnishes a new alkaloid *pyraconitine*, and this, on hydrolysis with water or acids, furnishes 1 mol. of benzoic acid and a new base *pyraconine.*

When a salt of aconitine is heated with water, a molecule of acetic acid is split off and the alkaloid *benzaconine*, which also occurs in aconite roots, and has been variously known as *picraconitine*, *isaconitine*, *napelline*, &c., is formed. Benzaconine, in turn, by hydrolysis with alkalis or acids, furnishes 1 mol. of benzoic acid, and the alkaloid *aconine*, which is the final basic product of the hydrolysis. Aconitine is therefore *acetylbenzoylaconine*.

On treatment with acetyl chloride aconitine furnishes a triacetyl derivative (m.p. 207°–208°). When heated with hydriodic acid it yields four mols. of methyl iodide, and must therefore contain four methoxyl groups. It also contains a methyl group linked to nitrogen. On oxidation with acid permanganate aconitine yields acetaldehyde and a neutral crystalline substance *oxonitine* (Carr, Chem. Soc. Trans. 1912, 101, 3241). This substance was also obtained by Brady (Chem. Soc. Trans. 1913, 103, 1821), and is most readily prepared by oxidation with permanganate in acetone solution (Barger and Field, Chem. Soc. Trans. 1915, 107, 231). The formula is most likely $C_{24}H_{29}O_9N$, m.p. 276°–277° (bath previously heated to 260°). Further oxidation with nitric acid yields a nitrosodicarboxylic acid $C_{22}H_{26}O_{11}N_2$, m.p. 205° (Brady). Oxonitine is also formed by the oxidation of japaconitine and deserves further investigation.

It is probable from the foregoing summary of the chief reactions of aconitine that it may be regarded as derived from a parent base $C_{20}H_{31}N$.



$$\left.\begin{matrix}AcO\\BzO\end{matrix}\right>C_{20}H_{21}NMe<\begin{matrix}(OH)_3\\(OMe)_4\end{matrix}$$

Aconitine.

Detection and estimation.—The identification of the alkaloid is best accomplished by the determination of the physical constants of its characteristic derivatives, but where minute quantities only are available the characteristic precipitate given with potassium permanganate (Dunstan and Carr, Pharm. J. 1896, [iv.] 2, 122), and the peculiar tingling sensation produced when even very dilute (1 in 4000) solutions of aconitine are applied to the tip of the tongue may be utilised, but these reactions are equally applicable to the 'aconitines' as a class. Various methods for the estimation of aconitine in aconite roots have been proposed, but, as a rule, these estimate some benzaconine and aconine as well as aconitine, and are useless as methods of determining the medicinal value of the roots, since this depends essentially on the amount of aconitine present. Aconitine itself may be estimated by hydrolysing it and determining the amount of acetic acid formed, but this method cannot be used for the estimation of aconitine in the plant since the latter contains other substances which yield acetic acid (Dunstan and Tickle, Pharm. J. 1896, [iv.] 2, 126).

Benzaconine $C_{32}H_{43}O_{10}N$ has also been called *isaconitine*, *picraconitine*, and *napelline* by various observers. It occurs with aconitine in aconite roots, and may be isolated from the mother liquors from which aconitine hydrobromide has been crystallised, and is also produced by heating an aqueous solution of an aconitine salt in a closed tube.

Properties. Amorphous, dextrorotatory base furnishing crystalline, lævorotatory salts. The hydrobromide crystallises in prisms, m.p. 273° (Schulze, *l.c.*); the hydrochloride occurs in two forms, m.p. 217° and 268° (Freund and Beck, Ber. 1894, 27, 729); the hydriodide has m.p 204°–205°. The aurichloride has m.p. 135°. According to Schulze (*l.c.*) the tetracetyl derivative of benzaconine is identical with triacetylaconitine.

With the removal of the acetyl group from aconitine the characteristic toxicity disappears and benzaconine is not toxic in the ordinary sense. In some respects its physiological action is antagonistic to that of aconitine (Cash and Dunstan, Phil. Trans. 1898, 190, 239).

Aconine $C_{25}H_{39}O_9N$, the ultimate basic product of the hydrolysis of aconitine or benzaconine is amorphous and dextrorotatory, but yields hygroscopic lævorotatory salts. It is readily soluble in water, alcohol, or chloroform, but almost insoluble in ether or light petroleum. The hydrochloride $B{\cdot}HCl,2H_2O$ has m.p. 175°–176°, and the hydrobromide $B{\cdot}HBr,1\frac{1}{2}H_2O$, m.p. 225°. The aurichloride is amorphous. The base furnishes a crystalline tetracetyl derivative, m.p. 231°–232° (Schulze, *l.c.* 1906, 244, 177). On oxidation with permanganate it furnishes acetaldehyde and an amorphous base, but with chromic acid it yields methylamine and two new bases $(OH)_4C_{20}H_{19}O(OMe)_3NMe$ and $C_{19}H_{20}O_4(OMe)_3(NMe){\cdot}CO_2H$, the former an amino alcohol and the latter an amino acid (Schulze, Arch. Pharm. 1908, 246, 281; *cf.* Carr, Proc. Chem. Soc. 1912, 28, 253; Brady, *ibid.* p. 289).

Bikhaconitine $C_{36}H_{51}O_{11}N$. The characteristic alkaloid of *Aconitum spicatum* (Stapf.), the roots of which constitute 'bikh'-aconite of North Western India. It may be extracted from the roots by a slight modification of the process described under aconitine. The alkaloid was isolated and characterised by Dunstan and Andrews (Chem. Soc. Trans. 1905, 87, 1636).

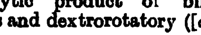
Properties. Separates from ether in button-shaped masses, m.p. 118°–123°, or from alcohol on addition of water in white granules containing $1H_2O$, m.p. 113°–116°. Dextrorotatory ($[\alpha]_D^{20°} = +12{\cdot}21°$ in alcohol). The salts are lævorotatory. The hydrochloride $B{\cdot}HCl,5H_2O$, m.p. 159°–161° (anhydrous), crystallises and has $[\alpha]_D -8{\cdot}86°$ (in water); the hydrobromide $B{\cdot}HBr,5H_2O$, m.p. 173°–175° (anhydrous) is crystalline and has $[\alpha]_D -12{\cdot}42°$; the hydriodide $B{\cdot}HI,2\frac{1}{2}H_2O$, m.p. 193°–194° (anhydrous), crystallises in needles, and is sparingly soluble in water; the aurichloride $B{\cdot}HAuCl_4$ crystallises in canary-yellow needles, m.p. 232°–233°. Like all the 'aconitines' bikhaconitine is highly toxic.

Reactions. Bikhaconitine contains six methoxyl groups. When heated at 180° it loses 1 mol. of acetic acid and forms pyrobikhaconitine (amorphous, giving amorphous salts). It undergoes hydrolysis in two stages, thus—

i. $\underset{\text{Bikhaconitine.}}{C_{36}H_{51}O_{11}N} + H_2O = \underset{\text{Veratroylbikhaconine.}}{C_{34}H_{49}O_{10}N} + \underset{\text{Acetic acid.}}{C_2H_4O_2}$

ii. $\underset{\text{Veratroylbikhaconine.}}{C_{34}H_{49}O_{10}N} + H_2O = \underset{\text{Bikhaconine.}}{C_{25}H_{41}O_7N} + \underset{\text{Veratric acid.}}{C_9H_{10}O_4}$

Bikhaconitine, therefore, resembles pseudaconitine (*see* p. 634) in furnishing veratric acid in the second stage of its hydrolysis. The alkaloid is, therefore, acetylveratroylbikhaconine, and may be represented thus—



$$[MeO]_4C_{21}H_{27}ON<\begin{matrix}OAc\\OVe\end{matrix}$$

Veratroylbikhaconine $C_{34}H_{49}O_{10}N$, the first basic hydrolytic product of bikhaconitine, is amorphous and dextrorotatory ($[\alpha]_D = +29{\cdot}9°$ in alcohol). The hydrochloride and hydrobromide are amorphous, but the hydriodide crystallises in rosettes of needles, m.p. 189°–190°. The nitrate forms rosettes of hexagonal prisms, m.p. 175°–178°. The aurichloride forms orange-yellow rosettes of prismatic crystals, m.p. 145°–148° (anhydrous).

Bikhaconine $C_{25}H_{41}O_7N$, the final basic product of the hydrolysis of bikhaconitine or veratroylbikhaconine. It is dextrorotatory and amorphous, but unlike the 'aconines' as a class, furnishes well-defined crystalline salts. The hydrochloride occurs in rosettes of crystals, m.p. 125°–130°, the hydrobromide in tetragonal prisms, m.p. 145°–150°, and the aurichloride

$$B{\cdot}HAuCl_4,3H_2O$$

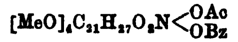
in glistening rhombic plates, m.p. 129°–132° (hydrated), or 187°–188° (anhydrous).

Indaconitine $C_{34}H_{47}O_{10}N$ is the characteristic alkaloid of *Aconitum chasmanthum* (Stapf.), a species indigenous to India, where it is known as 'Mohri.' It may be extracted from the roots by the process described under aconitine. The alkaloid was isolated and characterised by Dunstan and Andrews (Chem. Soc. Trans. 1905, 87. 1620).

Properties. Indaconitine crystallises in several characteristic forms, but can be obtained in crystals, which are almost identical in form with those of aconitine (*see* above). It has m.p. 202°–203°, and is dextrorotatory $[\alpha]_D = +18° 17'$. The salts crystallise well and are lævorotatory. The hydrochloride $B{\cdot}HCl,3H_2O$, m.p. 166°–171° (anhydrous), $[\alpha]_D = -15° 50'$, forms rosettes of silky needles; the hydrobromide, m.p. 183°–187° (anhydrous), $[\alpha]_D = -17° 16'$, crystallises from water in large hexagonal prisms; the aurichloride $B{\cdot}HAuCl_4,CHCl_3$, m.p. 147°–152°, forms rosettes of needles from chloroform by addition of ether.

Indaconitine gives a characteristic crystalline precipitate with potassium permanganate, the crystals being smaller and less stable than those given by aconitine. Like aconitine, indaconitine is highly toxic (Cash and Dunstan, Proc. Roy. Soc. 1905, B, 76, 468).

Reactions.—Indaconitine contains four methoxyl groups. On hydrolysis it behaves in a manner analogous to aconitine, yielding in the first stage acetic acid and indbenzaconine, the latter, on further hydrolysis, furnishing benzoic acid and pseudaconine. The latter is also the final basic hydrolytic product of pseudaconitine (p. 634), so that pseudaconitine differs only from indaconitine in containing a veratroyl group in place of a benzoyl group. Indaconitine is therefore acetylbenzoylpseudaconine, and may be represented thus—



$$[MeO]_4C_{21}H_{27}O_2N{<}^{OAc}_{OBz}$$

Indbenzaconine (Benzoylpseudaconine)

$$C_{32}H_{45}O_9N$$

the first basic product of the hydrolysis of indaconitine is amorphous and dextrorotatory, $[\alpha]_D = +33° 35'$, but furnishes well crystallised, lævorotatory salts. The hydrobromide

$$B{\cdot}HBr,2H_2O,$$

m.p. 247° (anhydrous) forms rosettes, the hydrochloride $B{\cdot}HCl$, m.p. 242°–244°, octahedra, and the aurichloride, m.p. 180°–182°, orange rosettes. The aurichloro derivative, m.p. 234°–235°, forms minute colourless crystals. On hydrolysis with alkalis indbenzaconine furnishes benzoic acid and pseudaconine (*see* p. 634). As is the case with aconitine the removal of the acetyl group virtually abolishes the toxicity of indaconitine and indbenzaconine is scarcely poisonous in the ordinary sense (Cash and Dunstan, *l.c.*).

Pyroindaconitine $C_{32}H_{42}O_8N$ exists in two forms. The α- form is produced when the free base, indaconitine, is heated at its melting-point. It is amorphous, but furnishes a crystalline hydrobromide $B{\cdot}HBr$, m.p. 194°–198°, which, like the alkaloid itself, is dextrorotatory. The aurichloride is amorphous. When indaconitine hydrochloride is heated at its melting-point it furnishes β-pyroindaconitine, which is also amorphous, but yields a crystalline hydrobromide, m.p. 248°–250°.

Japaconitine $C_{34}H_{49}O_{11}N$ is the characteristic alkaloid of Japanese aconite roots of commerce. It may be prepared from this source by the method described under aconitine. According to Makoshi the roots of true *Aconitum Fischeri* (Reichb.) contain jesaconitine (*see* below), whilst japaconitine is furnished by the roots of a variety grown in Hondo (Arch. Pharm. 1909, 247, 270), which Holmes regards as *A. uncinatum*, var. *japonicum*. Japaconitine has been frequently investigated, and up to 1900 the balance of evidence was in favour of the view that it was identical with aconitine (Mandelin, Arch. Pharm. 1885, 223, 97, 129, 161; Lübbe, Inaug. Diss. Dorp. 1891; and Freund and Beck, Ber. 1894, 27, 720. The non-identity of the two alkaloids had already been asserted by Wright and Luff (Chem. Soc. Trans. 1879, 35, 387), and was finally proved by Dunstan and Read (*ibid.* 1900, 77, 45). Their conclusions have been confirmed by Makoshi (*l.c.*).

Properties. Forms rosettes of prismatic needles, m.p. 204·2°, and is crystallographically distinct from aconitine and pseudaconitine. Dextrorotatory ($[\alpha]_D^{18{\cdot}5} = +23{\cdot}6°$ in alcohol), but furnishes lævorotatory salts. The hydrochloride $B{\cdot}HCl,3H_2O$, m.p. 149°–150°, $[\alpha]_D = -23{\cdot}8°$ in water, crystallises from alcohol and ether in rosettes of hexagonal plates; the hydrobromide $B{\cdot}HBr,4H_2O$, m.p. 172°–173°, crystallises similarly; the aurichloride exists in two modifications, the α- form, m.p. 231° is stable and crystallises in opaque, golden-yellow needles; the β- form, m.p. 154°–160°, is unstable and crystallises in yellow prisms. The physiological action of japaconitine is qualitatively identical with that of aconitine than which it is slightly more toxic (Cash and Dunstan, Proc. Roy. Soc. 1902, 68, 379).

Reactions. Japaconitine, unlike aconitine, reacts with methyl iodide to form a crystalline methiodide, and from this methyljapaconitine $C_{34}H_{48}O_{11}N{\cdot}CH_3$, m.p. 206°, rosettes of colourless needles may be obtained. Japaconitine forms a crystalline triacetyl derivative, m.p. 166°, and contains four methoxyl groups. When heated alone it furnishes 1 mol. acetic acid and 1 mol. pyrojapaconitine (*v. infra*). On hydrolysis it also behaves in a manner analogous to aconitine, giving first 1 mol. each of acetic acid and japbenzaconine. The latter may be further hydrolysed to benzoic acid and japaconine. Japaconitine is therefore acetylbenzoyljapaconine, and may be represented thus (D. a. R.)—

$$\begin{matrix}[HO]_3\\ [OMe]_4\end{matrix}{>}C_{21}H_{\ 5}NH{<}^{OAc}_{OBz}$$

Japbenzaconine $C_{32}H_{46}O_{10}N$, the first basic hydrolytic product of japaconitine, also occurs with this alkaloid in Japanese aconite roots. Unlike the analogous benzaconine, it crystallises, though with difficulty, m.p. 183°. Dextrorotatory ($[\alpha]_D = +40{\cdot}16°$ in alcohol). The salts crystallise well, and are lævorotatory; the hydrochloride $B{\cdot}HCl,H_2O$, m.p. 253°, forms minute rosettes; the aurichloride $B{\cdot}HAuCl_4$ crystallises from alcohol and then melts at 219°. The colourless aurichloro derivative

$$C_{32}H_{46}O_{10}N{\cdot}AuCl_2,$$

m.p. 178°, forms rosettes of needles (D. a. R. *l.c.*).

Japaconine $C_{25}H_{43}O_9N$, the final basic product of the hydrolysis of japaconite or japbenzaconine, is amorphous, and hygroscopic and yields hygroscopic salts, which crystallise with difficulty. Its solutions reduce gold chloride and Fehling's solution. The base is dextrorotatory (D. a. R. *l.c.*).

Pyrojapaconitine $C_{32}H_{45}O_9N$ is formed by heating japaconite at its melting-point, when 1 mol. of acetic acid is evolved. Crystallises in colourless needles, m.p. 167°–168°, is lævorotatory ($[\alpha]_D = -65{\cdot}89°$ in alcohol), and furnishes well-crystallised salts; the aurichloride

$$B{\cdot}HAuCl_4,$$

m.p. 160°–161° (from chloroform), or 188°–189° (from alcohol and ether). On hydrolysis by alkalis the base gives rise to 1 mol. benzoic acid and a new base *pyrojapaconine*, which is amorphous, hygroscopic, and lævorotatory, and furnishes amorphous salts.

According to Schulze and Liebner (Arch. Pharm. 1913, 251, 453; 1916, 254, 567), pyrojapaconitine $C_{32}H_{43}O_9N$, m.p. 171°, and pyrojapaconine are identical with pyraconitine and pyraconine respectively. As aconitine and japaconitine both give oxonitine (*q.v.*) on oxidation, these two alkaloids must be closely related.

Jesaconitine $C_{40}H_{51}O_{12}N$, isolated by Makoshi (Arch. Pharm. 1909, 247, 251) from '[illegible]ushi' roots obtained from a species of aconite, A. *Fischeri* (?), found in the island of Hokkaido or Jeso in Japan. It was not obtained crystalline, but a crystalline triacetyl derivative, m.p. 213°, was prepared. On hydrolysis jesaconitine yielded benzoic acid, anisic acid, and aconine, identical with that obtained from aconitine, so that it is regarded as benzoylanisoylaconine. Jesaconitine is highly toxic (Makoshi, *l.c.*).

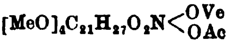
Lappaconitine $C_{34}H_{48}O_8N_2$, obtained by Rosendahl (J. Pharm. Chim. 1896, [vi.] 4, 262) from the roots of *Aconitum septentrionale* (Koelle). It crystallises in hexagonal prisms, m.p. 205°, is dextrorotatory, shows a reddish-violet fluorescence in ether, and furnishes crystalline salts. On hydrolysis it yields two bases; one, m.p. 98°, readily soluble, and the other, m.p. 106°, nearly insoluble in ether; at the same time an acid, m.p. 114°, giving a purple colour with ferric chloride, is produced. Lappaconitine is highly toxic. The roots also contain *cynoctonine* $C_{36}H_{55}O_{13}N_2$ (amorphous, bitter, and much less toxic than lappaconitine) and *septentrionaline* $C_{31}H_{48}O_9N_2$, amorphous, bitter, and about equal in toxicity to cynoctonine (*cf.* Orloff, P. Z. f. R. 1907, 36, 213).

Lycaconitine $C_{36}H_{46}O_{10}N_2$, obtained by Dragendorff and Spohn (P. Z. f. R. 1884, 23, 313) and later by Schulze and Bierling (Arch. Pharm. 1913, 251, 8) along with *myoctonine* ($C_{36}H_{42}O_{10}N_2$) and an unnamed base, from the roots of *Aconitum Lycoctonum* (Linn.), is amorphous and dextrorotatory. On hydrolysis with acids it furnishes anthranoyl-lycoctonine (Dragendorff's lycaconine) and succinic acid. On hydrolysis with sodium hydroxide lycoctonine $C_{25}H_{39}O_7N,H_2O$ and lycoctoninic acid $C_{11}H_{13}O_5N$, both crystalline, are formed. Lycoctonine had been found previously by Hübschmann in the roots (J. 1857, 416; 1866, 483; *cf.* Wright and Luff, Pharm. J. 1878–9, [iii.] 8, 169). All the alkaloids described are heart poisons.

Pseudaconitine $C_{36}H_{51}O_{12}N$. The characteristic alkaloid of *Aconitum deinorrhizum*, the roots of which form Nepaul aconite of commerce. It may be extracted from the roots by the process described under aconitine. Pseudaconitine has been frequently examined (Wright and Luff, Chem. Soc. Trans. 1878, 33; 151; Mandelin, Arch. Pharm. 1884, 222, 97, 129, 161), and most recently by Dunstan and Carr (Chem. Soc. Proc. 1895, 154; and Chem. Soc. Trans. 1897, 71, 350).

Properties. Colourless crystals of rhomboidal shape, m.p. 211°–212° (decomp.); $[\alpha]_D = +18\ 30'$ in alcohol. Readily soluble in alcohol, less so in ether, very slightly in water, almost insoluble in light petroleum. The salts are lævorotatory; the hydrobromide $B{\cdot}HBr,2H_2O$, m.p. 191° (anhydrous), and the nitrate $B{\cdot}HNO_3,3H_2O$, m.p. 192°, are crystalline. The hydrochloride is amorphous, but the aurichloride, m.p. 235°–236°, may be crystallised from alcohol. Pseudaconitine exerts a physiological action similar to that of aconitine, but is much more toxic (Cash and Dunstan, Proc. Roy. Soc. 1902, 68, 379).

Reactions. On heating an aqueous solution of a neutral pseudaconitine salt in a closed tube at 135° the alkaloid undergoes hydrolysis, yielding 1 mol. acetic acid and 1 mol. veratroylpseudaconine. The latter is hydrolysed in the cold by sodium hydroxide in alcohol, furnishing 1 mol. of veratric acid and 1 mol. of pseudaconine. When heated at its melting-point pseudaconitine loses 1 mol. acetic acid and furnishes pyropseudaconitine. Pseudaconitine, in view of these reactions, is to be regarded as acetylveratroylpseudaconine



$$[MeO]_4C_{21}H_{27}O_2N{<}{\substack{OVe\\OAc}}$$

No relationship has yet been traced between pseudaconine and aconine (D. a. C.; *cf.* Freund and Niederhofheim, Ber. 1896, 29, 6, 852).

Veratroylpseudaconine $C_{34}H_{49}O_{11}N$. The first basic product of the hydrolysis of pseudaconitine (*see* above) separates in large, irregularly-shaped crystals from ether, m.p. 199°, readily soluble in chloroform or alcohol, nearly insoluble in water or light petroleum, $[\alpha]_D = -38°\ 18'$ in alcohol. The salts crystallise well; the hydrobromide $B{\cdot}HBr,3H_2O$ in prisms; the nitrate $B{\cdot}HNO_3$ in rosettes of rhombic prisms, m.p. 222° and 232°; the aurichloride $B{\cdot}HAuCl_4$ is amorphous (D. a. C.). Veratroylpseudaconine is not toxic (Cash and Dunstan, *l.c.*).

Pseudaconine $C_{25}H_{41}O_8N$, the ultimate basic product of the hydrolysis of pseudaconitine and indaconitine, forms large colourless crystals, m.p. 94°–95°, containing 1 mol. alcohol of crystallisation. Dextrorotatory ($[\alpha]_D = 38° 12'$ in water). The salts are amorphous.

Pyropseudaconitine $C_{34}H_{47}O_{10}N$. Formed by heating pseudaconitine at its melting-point, when 1 mol. acetic acid is evolved; it is amorphous, but yields a hydriodide, crystallising in prisms (D. a. C. *l.c.*).

Atisine $C_{22}H_{31}O_2N$, the characteristic alkaloid of *Aconitum heterophyllum* (Wall.) of Northern India. It was first isolated by Broughton in 1873, and was subsequently examined by Wasowicz (Arch. Pharm. 1879, 214, 193), Wright (Year Book Pharm. 1879, 422), and later by Jowett (Chem. Soc. Trans. 1896, 69, 1518). Atisine is amorphous, readily soluble in water, alcohol, ether, or chloroform, lævorotatory ($[\alpha]_D^{19°} = -19.6°$ in alcohol). It yields crystalline, dextrorotatory salts; $B \cdot HCl$, prisms, m.p. 296° (decomp.); $B \cdot HI$, tablets, m.p. 279°–281° (decomp.); $B_2 \cdot H_2PtCl_6$, crystalline yellow powder, m.p. 229° (decomp.). When heated with water in a closed tube atisine furnishes a *hydrate* $C_{22}H_{33}O_3N$, which is amorphous, and yields amorphous salts. Atisine is non-toxic (Jowett, *l.c.*).

Palmatisine. A colourless, crystalline, non-toxic alkaloid, m p. 285°, found in the roots of *Aconitum palmatum* (D. Don.), a species indigenous to India (Dunstan and Carr).

The fullest account of the aconite alkaloids is by F. H. Carr, in Allen's Commercial Organic Analysis, vol. vi. 1912, pp. 253-287. G. B.

ACORN OIL. Although acorn oil has not yet become a commercial article, the yield of oil obtainable would repay the cost of collecting the acorns, while the oil-cake would furnish a valuable feeding stuff. Baker and Hulton (Analyst, 1917, 42, 351) found that a ton of fresh acorns from *Quercus robur* yielded, on the average, 16·75 cwt. of kernels, corresponding to 8·5 cwt. of dry kernels. Two specimens of peeled acorns had the following composition: Moisture, 1·45 and 3·32; ash, 2·25 and 2·70; oil, 5·0 and 4·7; proteins, 6·65 and 7·75; reducing sugars, 4·9 and 8·18; cane sugar, 1·9 and 0·1; starch, 57·1 and 55·7; pentosans, 3·2; and crude fibre, 2·2 and 2·28 p.c. By hydrolysing the crushed nuts with dilute sulphuric acid, and neutralising and fermenting the filtrate 12·7 p.c. of alcohol (calculated on the fresh acorns) was obtained. Acorns, unlike chestnuts, do not appear to contain a liquefying enzyme.

An oil extracted from the acorns of *Q. agrifolia* was fluorescent and of a deep brown colour. It had sp.gr. 0·9162 at 15°, and iodine value 100·6, and belonged to the same type of oils as arachis oil (Blasdale, J. Amer. Chem. Soc. 1895, 17, 935). C. A. M.

ACORUS CALAMUS (Linn.). The common sweet flag. The root is used by distillers to flavour gin, and the essential oil by snuff-makers for scenting snuff. It contains a glucoside termed *acorin* $C_{36}H_{60}O_6$ (Faust, Bull. Soc. chim. [2] 9, 392; Thoms, Arch. Pharm. [3] 24, 465) (*v.* CALAMUS).

ACRIDINE $C_{13}H_9N$. Crude anthracene contains basic substances, and among them acridine, which can be isolated by extracting it with dilute sulphuric acid and adding potassium dichromate to the acid solution. The precipitated acridine chromate is then recrystallised from water, treated with ammonia, and the base crystallised from hot water (Graebe and Caro, Annalen, 158, 265; Ber. 13, 99).

Acridine has also been obtained synthetically by passing the vapours of orthotolylaniline and of orthoditolylamine through a tube heated to dull redness (G., Ber. 17, 1370); by severally heating formic acid and diphenylamine (Bernthsen and Bender, Ber. 16, 767, 1802), chloroform, diphenylamine and zinc oxide (Fischer and Körner, Ber. 17, 101), and aniline and salicylaldehyde (Möhlau, Ber. 19, 2451) with zinc chloride; by passing *o*-amidodiphenyl methane through a layer of lead oxide heated to dull redness (Fischer and Schütte, Ber. 26, 3085). By distilling tetrahydroacridine with litharge (Borsche, Ber. 41, 2203), and also from acridone (Decker and Dunant, Ber. 39, 2720; Ullmann, Bader and Labhardt, Ber. 40, 4795).

From iodobenzene and *o*-aminobenzaldehyde boiled with nitrobenzene, sodium carbonate and copper powder (Mayer and Stein, Ber. 1917, 50, 1306).

Properties.—Acridine crystallises in small colourless needles, or four-sided rhombic prisms, sublimes at 100°, melts at 111°, boils above 360° without decomposition, and distils with steam. It is sparingly soluble in hot water, but readily soluble in alcohol, ether, or carbon disulphide, yielding solutions showing a blue fluorescence. When inhaled either as dust or vapour it causes violent sneezing, and in solution both it and its salts cause much irritation on the skin. On treatment with nitric acid it yields two nitro-derivatives (m.p. 154° and 214°) and a dinitro-derivative (G. and C.); potassium permanganate oxidises it to 2:3-quinolinedicarboxylic acid $C_9H_5N(CO_2H)_2$, and sodium amalgam reduces it to *hydroacridine* $C_{13}H_{11}N$ (B. and B., Ber. 16, 1971; B., Ber. 16, 2831). The salts are yellow and crystallise well, but are decomposed into their constituents on boiling. Heated with hydrogen and finely divided nickel, it forms 2:3-dimethyl quinoline (Padoa and Fabris, Atti R. Acad. Lincei, 1907, [v.] 16, i. 921). The halogen addition compounds of acridine and its derivatives are formed by the direct action of the halogen on the acridine (Senier and Austin, Chem. Soc. Trans. 1904, 1196); or by the action of a mixture of phosphorus oxychloride and pentachloride on thioacridone (Edinger, Ber. 33, 3370; D. R. P. 120586; Edinger and Arnold, J. pr. Chem. [ii.] 64, 182, 471; D. R. P. 122607); for other methods, compare Dunstan and Stubbs (Ber. 39, 2402; D. R. P. 126795), Graebe and Lagodzinski (Annalen, 276, 48). Alkyl iodomagnesium compounds of acridine have also been obtained (Senier, Austin, and Clarke, Chem. Soc. Trans. 1905, 1469). When exposed to sunlight acridine forms pale-yellow crystals, m.p. 276° (Orndorff and Cameron, Amer. Chem. J. 1895, 17, 558).

3:7-dimethyl-2:8-diaminoacridine[1] or *acri-*

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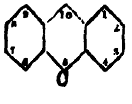
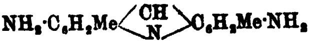
[1] The system of numbering the positions in the acridine series adopted in this article and in that on the "Acridine Dyestuffs," is that used in Richter's *Lexikon* viz.:



dine yellow  $NH_2\cdot C_6H_2Me\left\langle {}^{CH}_{N} \right\rangle C_6H_2Me\cdot NH_2$ is obtained by heating under pressure tetraminoditolylmethane with hydrochloric acid and water, the product is then oxidised with ferric chloride or potassium percarbonate $K_2C_2O_6$ or hydrogen peroxide, and the resulting metallic salt decomposed with hydrochloric acid (D. R. P. 52324; Lymn, J. Soc. Chem. Ind. 1897, 16, 406; Ullmann and Marić, Ber. 34, 4308; Haase, Ber. 36, 589). It forms yellow crystals melting above 300°, soluble in alcohol, acetone and pyridin, and forming a yellow solution in sulphuric acid with a green fluorescence. It yields derivatives which form yellow, orange, brownish-, greenish-, and reddish-yellow dyes, and can be used on cotton, leather, wool, and silk. The following are some of the methods of preparation: (1) heating with mineral acids under pressure, when it yields aminohydroxy- and dihydroxydimethyl acridine (D. R. P. 121686; Chem. Zentr. 1901, ii. 78; J. Soc. Chem. Ind. 21, 37); (2) heating with monochloracetic acid and water under pressure (D. R. P. 133788; Chem. Zentr. 1902, ii. 616; D. R. P. 136729; Chem. Zentr. 1902, ii. 1396); (3) heating with formaldehyde and mineral acids under pressure (D. R. P. 135771; Chem. Zentr. 1902, ii. 1233; J. Soc. Chem. Ind. 21, 112, 544, 402); (4) by treatment with formaldehyde and aromatic bases (J. Soc. Chem. Ind. 22, 140; D. R. PP. 131365, 132116; Chem. Zentr. 1902, ii. 172; i. 1288); (5) heating with benzyl chloride in presence of nitrobenzene (J. Soc. Chem. Ind. 21, 701, 1530); (6) treating with aqueous formic acid (*ibid.* 21, 90); (7) heating with glycerol at 150°–180° (D. R. P. 151206): (8) alkylation (Ullmann and Marić, *l.c.*; D. R. P. 79703; J. Soc. Chem. Ind. 19, 1010; 24, 840).

Phenylacridine $C_{19}H_{13}N$ is obtained by heating diphenylamine with benzoic acid and zinc chloride at 260° (Bernthsen, Ber. 16, 3012; 16, 767, 1810), and melts at 181°. The *hydroxyphenylacridines* which form yellow dyes in mineral acids can be obtained similarly by using the corresponding hydroxy acid (Landauer, Bull. Soc. chim. 31, 1083).

Other acridine dyes can be obtained by heating tetraminoditolylmethane or the leuco-compounds of amino-acridines with mineral acid and alcohol under pressure, the shade depending on the quantity and nature of alcohol and of acid used (J. Soc. Chem. Ind. 20, 888; 22, 1126; 23, 932). Also by the interaction of an aromatic or aliphatic *m*-diamine with an aldehyde (*ibid.* 21, 1529; Chem. Zeit. 14, 334; J. Soc. Chem. Ind. 17, 573; 22, 1211). By heating the formyl derivatives of *m*-diamines with ammonia salts or salts of organic bases at 150°–200° (D. R. PP. 149409, 149410). For other methods of preparing acridine derivatives, many of which have dyeing properties, compare: Bizzarri, Gazz. chim. ital. 20, 407; Decker, J. pr. Chem. 153, 161; Mohlau and Fritzsche, Ber. 26, 1034; Volpi, Gazz. chim. ital. 21, ii. 228; J. Soc. Chem. Ind. 19, 732; 21, 338, 701, 911, 1528; Goodwin and Senier, Chem. Soc. Trans. 1902, 285; J. Soc. Chem. Ind. 22, 23, 90; D. R. PP. 133709, 107517; Ullmann, Ber. 36, 1017, 1025; D. R. P. 141297, 141356; Bünzley and Decker, Ber. 37, 575; Fox and Hewitt, Chem. Soc. Trans. 1904, 529; 1905, 1058; Schöpff, Ber. 26, 1121; Ber. 27, 2316; Duval, Compt. rend. 142, 341; Koenigs, Ber. 32, 3599; Ullmann and Maag, Ber. 40, 2515; Austin, Chem. Soc. Trans. 1908, 1760; D. R. PP. 118075, 152662; Pope and Howard, Chem. Soc. Trans. 97, 83.

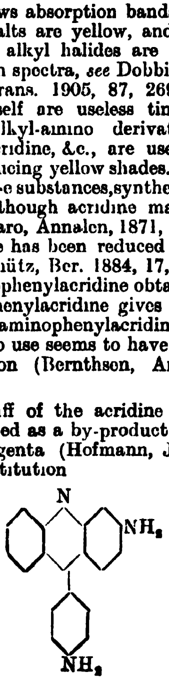
Naphthacridine and its derivatives, which can also be used as dyes, have been prepared (J. Soc. Chem. Ind. 18, 826; 19, 237; Ullmann and Naef, Ber. 33, 905, 912, 2470; J. Soc. Chem. Ind. 20, 37, 573; D. R. P. 126444; Ullmann and Baezner, Ber. 35, 2670; 37, 3077; Ullmann and Felzvadjian, *ibid.* 36, 1027; Ullmann and Farre, *ibid.* 37, 2922; Ullmann and Fitzenham, *ibid.* 38, 3787; Baezner and Gardiol, *ibid.* 39, 2623; Baezner, *ibid.* 2650; Senier and Austin, Chem. Soc. Trans. 1907, 1233, 1240; Senier and Compton, *ibid.* 1907, 1927; Baezner and Gueorgnieff, Ber. 39, 2438).

In the case of many of the naphthacridine derivatives, patents have been taken by Ullmann (D. R. PP. 104667, 104748, 108273, 117472, 119573, 123260, 127586, 128754, 130721, 130943); the further alkylation of some of these, as well as of other acridine compounds has been patented by the A.-G. für Anilin-Fabrikation (D. R. PP. 117065, 129479).

ACRIDINE DYESTUFFS. Acridine, though colourless, shows absorption bands in the ultraviolet. The salts are yellow, and the addition products with alkyl halides are also coloured. (For absorption spectra, *see* Dobbie and Tinkler, Chem. Soc. Trans. 1905, 87, 269.) The salts of acridine itself are useless tinctorially, but amino- and alkyl-amino derivatives of acridine, phenylacridine, &c., are useful dyestuffs, generally producing yellow shades. For the preparation of these substances, synthesis is generally resorted to, although acridine may be nitrated (Graebe and Caro, Annalen, 1871, 158, 275), and *a*-nitro-acridine has been reduced to an amino-acridine (Anschütz, Ber. 1884, 17, 437).

The trinitrophenylacridine obtained by direct nitration of phenylacridine gives a dyestuff on reduction (? triaminophenylacridine), which dyes silk yellow; no use seems to have been made of this observation (Bernthsen, Annalen, 1884, 224, 30).

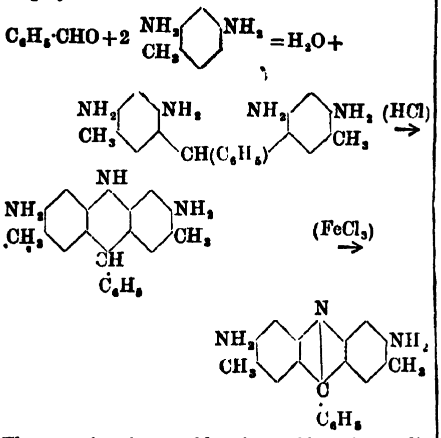
One dyestuff of the acridine series, *chrysaniline*, is formed as a by-product in the manufacture of magenta (Hofmann, Jahresb. 1862, 346). Its constitution



was determined by O. Fischer and G. Körner; probably two molecules of aniline and one of *p*-toluidine condense when oxidised to *opp*-triaminotriphenylmethane, this yielding chrysaniline when further oxidised. This view is supported by the fact that when *opp*-triaminotriphenylmethane is heated with arsenic acid to 150°–180°, chrysaniline is produced (Annalen, 1884, 226, 188).

The processes for preparing amino- derivatives of acridine on a technical scale may be illustrated by the methods of preparing *benzoflavine*, *rheonine*, and *diaminoacridylbenzoic acid*.

Symmetrical diamino-acridines are obtained by the condensation of aldehydes with *m*-diamines, removal of the elements of ammonia from the resulting tetra-amino- compound by heating with hydrochloric acid, and oxidation of the dihydro-acridine thus produced with ferric chloride. In the case of *benzoflavine* benzaldehyde and *m*-toluylene-diamine are employed.



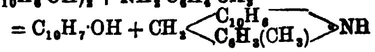
The reaction is capable of considerable modification; thus from formaldehyde and dimethyl-*m*-phenylenediamine, *acridine orange* is produced in an analogous manner. It should be noted, however, that *m*-phenylenediamine gives products which are evidently mixtures, and cannot be purified (R. Meyer and R. Gross, Ber. 1899, 32, 2365).

Diaminoacridine may, however, be obtained from *pp*′-diamino-diphenylmethane (*see* below).

The reaction between an aldehyde and a *m*-diamine may be carried out in two stages; Meyer and Gross (*l.c.* p. 2358), for example, prepared a monobenzylidene derivative of *m*-toluylenediamine and converted this into tetraminoditolyl-phenylmethane by warming its alcoholic solution with the hydrochloride of *m*-toluylenediamine for three hours at 60°–70°. Acridine itself may be obtained in good yield by heating salicylidene-aniline with phosphorus pentoxide to 250° (Blau, Monatsh. 1897, 18, 123).

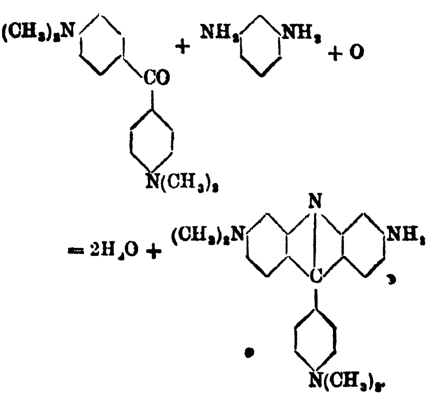
A closely-related synthesis of acridine derivatives is that of F. Ullmann and E. Naef (Ber. 1900, 33, 905). When dihydroxydinaphthylmethane, the product of the interaction of formaldehyde and *β*-naphthol, is heated with *p*-toluidine hydrochloride, methylhydronapthacridine is produced with elimination of *β*-naphthol.

$$CH_2(C_{10}H_6·OH)_2 + NH_2·C_6H_4·CH_3$$

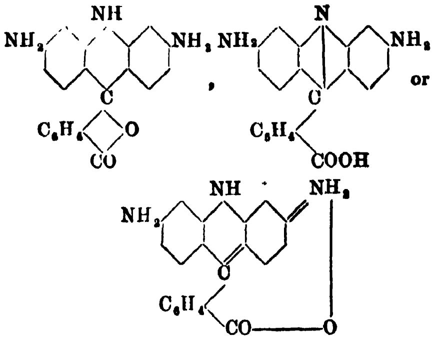


$$= C_{10}H_7·OH + CH_2\begin{cases}C_{10}H_6 \\ C_6H_3(CH_3)\end{cases}NH$$

Rheonine is obtained from *m*-aminophenylauramine or tetramethyldiaminobenzophenone and *m*-phenylenediamine at 200°, using zinc chloride as condensing agent.



Some derivatives of xanthene, when energetically treated with ammonia, suffer replacement of the pyrone oxygen atom by an imino-group. By the prolonged heating of fluorescein with ammonia under pressure, R. Meyer (Ber. 1888, 21, 3376) obtained an acridine derivative, to which one of the three following constitutions is assignable:—



The salts of the tetra-ethyl derivative of this compound form the dyestuff known as *flaveosine*.

Acridine Orange NO (Farbwerk Mühlheim, D. R. P. 59179, 17 Dec. 1889), $C_{13}H_7N[N(CH_3)_2]_2·HCl·ZnCl_2$ was discovered by Bender. It is produced by condensation of dimethyl-*m*-phenylenediamine with formaldehyde and proceeding according to the method referred to above. It forms an orange powder which dissolves in water or alcohol with orange-red colour and greenish fluorescence. The aqueous solution is reddened by hydrochloric acid; sodium hydroxide gives a yellow precipitate. The solution in concentrated sulphuric acid is nearly colourless and has a greenish fluorescence, dilution with water produces successively red and orange colouration. The dye gives orange shades, fairly fast to light and soap, on cotton mordanted with tannin; it is also suitable for printing and leather-dyeing.

The analogous dyestuff from diethyl-*m*-phenylenediamine is described in D. R. P. 67609, the substances derived from monoalkylphenylenediamines in D. R. P. 70935.

Another method of preparing acridine orange is to heat 12 kilos. of aminodimethylaniline either with 10 kilos. of formic acid (sp.gr. 1·2) and 10 kilos. of zinc chloride gradually to 150°–160°, or with 12 kilos. of dehydrated oxalic acid, 10 kilos. of glycerol and 11 kilos. of zinc chloride to 150°. Heating and stirring are continued as long as any darkening of shade can be observed, ammonia is liberated during the reaction, and formic acid having been employed instead of formaldehyde, the product when worked up yields the dyestuff instead of its leuco-compound (D. R. P. 67126).

The formyl derivatives of *m*-diamines may also be used (D. R. PP. 149049, 161699), or the 'methane' carbon atom may be furnished by various formyl derivatives such as formanilide (D. R. P. 149410).

Acridine Orange, R extra (Farbwerk Mühlheim, D. R. P. 68908, 7 Feb. 1890). The dyestuff is the hydrochloride of tetramethyldiamino-5-phenylacridine, and is obtained from dimethyl-*m*-phenylenediamine and benzaldehyde. Its reactions and uses are similar to those of Mark NO.

D. R. P. 68908 also mentions the use of *m*-aminodimethyl-*o*-toluidine. If the latter base be condensed with *p*-nitrobenzaldehyde to a triphenylmethane derivative, the nitro- group reduced and condensation and oxidation effected in the usual way, an acridine dyestuff possessing two tertiary and one primary amino- group is obtained (D. R. P. 70065; compare D. R. P. 71362).

The use of acetaldehyde as a component was claimed by the Ges. f. Chem. Ind. (D. R. P. 143893, 13 March, 1902).

Acridine Yellow (Farbwerk Mühlheim, D. R. P. 52324, 27 June, 1889) was, like the two preceding colours, discovered by Bender. Its constitution is that of a 2 : 8-diamino-3 : 7-dimethylacridine hydrochloride; it is produced from formaldehyde and *m*-toluylenediamine. It forms a yellow powder soluble in water and alcohol with yellow colour and green fluorescence; yellow precipitates are obtained with hydrochloric acid (hydrochloride) and sodium hydroxide (free base). Silk is dyed a greenish yellow with green fluorescence, cotton (tannin mordant) is coloured yellow.

The salts with aliphatic acids, *e.g.* formate and acetate, are more soluble (Farbenfabriken vorm. F. Bayer, D. R. P. 140848, 13 March, 1903). Acridine yellow is converted into an orange yellow, more easily soluble dyestuff by heating with twice its weight of glycerol for 4–6 hours to 170°–180° (Badische Anilin und Soda-Fabrik, D. R. P. 151206, 26 July, 1903).

(For the action of aldehyde on aniline yellow, *see* D. R. P. 144092.) Compounds, probably of acridinium type, are obtained from aniline yellow by the action of monochloracetic acid (M. L. B., D. R. PP. 133788, 136729, 152662) and other dyestuffs by condensation with formaldehyde and *m*-diamines (D. R. PP. 131365, 132116, 135771). Either one or both of the amino- groups in acridine yellow and analogous dyestuffs are replaced by hydroxyl on heating with dilute sulphuric acid to 180°–220° (D. R. P. 121686), and similar compounds may be obtained from formaldehyde by condensation with amino-cresols (D. R. P. 120466).

Dibenzyl aniline yellow is claimed by Bayer & Co. as a useful leather dye (D. R. P. 141297).

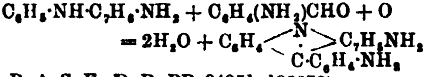
Benzoflavine (several marks) 2 : 8-diamino-3 : 7-dimethyl-5-phenylacridine hydrochloride $C_{13}H_4N(C_6H_5)(NH_2)_2(CH_3)_2,HCl$, was discovered by Rudolph in 1887, and introduced commercially by K. Oehler in 1888 (D. R. PP. 43714, 28 July, 1887; 43720, 45264, 45298). Its preparation has been given above. The dye, which is usually mixed with dextrin, forms an orange powder, difficultly soluble in cold water, more easily in hot. Both aqueous and alcoholic solutions are orange, with strong green fluorescence. Hydrochloric acid gives an orange precipitate, sodium hydroxide liberates the yellowish-white base. The solution in concentrated sulphuric acid is greenish yellow, and shows a very strong green fluorescence. It may be used for dyeing both mordanted and unmordanted cotton. The acetate and lactate are more readily soluble (Bayer, D. R. P. 142453, 19 April, 1902); it behaves like acridine yellow when heated with glycerol.

The **Patent Phosphines** of the Ges. f. Chem. Ind. in Basel are obtained by alkylation of benzoflavine and acridine yellow (D. R. P. 79703; compare D. R. P. 131289).

Coriophosphines (Bayer & Co.). These dyestuffs, which are suitable for leather-dyeing, are probably unsymmetrically alkylated diamino-acridines obtained by condensation of formaldehyde with one molecule of an asymmetrically dialkylated *m*-diamine and one molecule of a non-alkylated or monoalkylated *m*-diamine, with subsequent elimination of ammonia, and oxidation (D. R. P. 133709).

Chrysaniline $C_{19}H_{15}N$ occurs under many other names commercially, *e.g.* Leather yellow, Xanthine, Philadelphia yellow G, Leather brown, Phosphine (several marks), &c. Reference to its occurrence in the manufacture of magenta has already been made. Numerous methods for preparing homologues and analogues of this substance have been patented (D. R. PP. 65985, 78377, 79263, 79585, 79877, 81048, 94951, 102072, 106719, 114261, 116353). The method adopted for this purpose by Meister, Lucius, and Brüning may be mentioned (D. R. P. 65985, 2 April, 1892). *p*-Toluidine and its hydrochloride are heated with ferric chloride (oxygen-carrier), and *m*-nitroaniline gradually added. The resulting dyestuff is the next higher homologue of chrysaniline, containing a methyl- group in position 7.

According to Friedländer (Fortschritte der Theerfarbenfabrikation V. 373), the yields produced by this method are not good, but the reaction between *p*-aminobenzaldehyde or a derivative and phenyl-*m*-phenylene- (or toluylene-) diamine proceeds nearly quantitatively:



$$C_6H_5{\cdot}NH{\cdot}C_7H_6{\cdot}NH_2 + C_6H_4(NH_2)CHO + O$$
$$= 2H_2O + C_6H_4\left<\begin{matrix} N \\ \vdots \\ C{\cdot}C_6H_4{\cdot}NH_2 \end{matrix}\right>C_7H_5NH_2$$

B. A. S. F., D. R. PP. 94951, 102072).

Chrysaniline forms an orange-yellow powder, soluble in water and alcohol with reddish-yellow colour and yellowish-green fluorescence. The solution is unaltered by hydrochloric acid; sodium hydroxide gives a bright yellow precipitate. Chrysaniline is chiefly used in leather dyeing.

Corioflavines (Griesheim-Elektron). These dyestuffs, which occur commercially as marks G, GG, R, and RR, are used in leather-dyeing and calico-printing. They form red or reddish-brown powders, which dissolve in concentrated sulphuric acid with yellow or orange colouration and green fluorescence; these solutions turn red or reddish-brown on dilution.

Flaveosine (Meister, Lucius, and Brüning, D. R. P. 49850, 11 May, 1889) is a tetraethyldiaminoacridylbenzoic acid, which is obtained by heating *m*-acetaminodimethylaniline with phthalic anhydride. It has been examined by Grandmougin and Lang (Ber. 1909, 42, 4014).

The hydrochloride crystallises in shining brownish-yellow needles, the sulphate in prisms exhibiting a cantharides lustre. The base is precipitated from the salts by sodium carbonate, and forms golden-yellow shining leaflets.

Flaveosine dyes silk golden yellow (yellowish-green fluorescence) from a feebly acid bath; wool and cotton (tannin mordant) are coloured reddish yellow. The colours are fast.

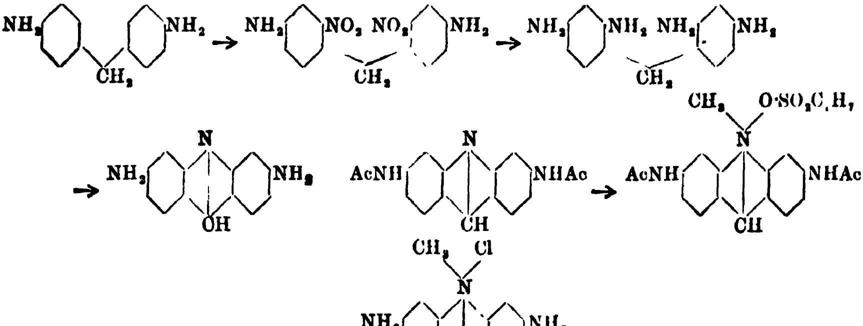
Substances closely related to flaveosine are obtained by the esterification of the product of the interaction of ammonia and fluorescein (B. A. S. F., D. R. PP. 73334, 75933; compare D. R. P. 141356).

Rheonine (Badische Anilin und Soda-Fabrik). This dyestuff was discovered by C. L. Müller (D. R. P. 82989, 16 Dec. 1894). Its method of preparation has already been given. Rheonine forms a brown powder, soluble in water and alcohol, with brownish-yellow colour and green fluorescence. Hydrochloric acid turns the solution brownish-red, caustic soda gives a bright brown precipitate. It is used for obtaining brownish-yellow shades on leather or cotton (tannin). Two marks, N (brighter), and A (darker), are in use.

The use of diaminobenzophenone and of Michler's hydrol for condensation with *m*-diamines have been patented (M. L. B., D. R. P. 89660 and B. A. S. F., D. R. P. 85199 respectively).

Many acridine and naphthacridine dyestuffs containing only one amino- group have been described (D. R. PP. 104667, 107517, 107626, 108273, 118075, 118076, 125697, 130360); and it has also been observed that dyestuffs can be obtained when only one molecular proportion of a *m*-diamine is used with formaldehyde (D. R. P. 136617).

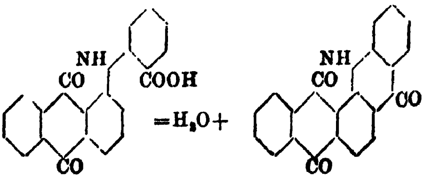
Trypaflavine. The 2 : 8-diamino-10-methylacridonium salts first acquired interest on account of their trypanocidal action (L. Benda, Ber. 1912, 45, 1787). As mentioned above, the condensation of aldehydes with *m*-phenylenediamine gives a mixture of substances. If *pp*′-diamino-diphenylmethane is nitrated in cold sulphuric acid solution, *oo*′-dinitro-*pp*′-diaminodiphenylmethane is produced. The latter compound by reduction with tin and hydrochloric acid and heating the resulting solution for four hours at 135° gives the stannichloride of 2 : 8-diaminoacridine (L. Cassella & Co. D. R. P. 230412). After acetylation of the amino-groups, the nitrogen atom of the pyridine nucleus may be methylated by means of methyl toluene-sulphonate and the acetyl groups subsequently removed by heating with a mixture of equal volumes of water and hydrochloric acid (*e.g.* 1·18). The steps in the formation of trypaflavine may be represented thus:—



The reactions of trypaflavine have been studied by Ehrlich and Benda (Ber. 1913, 46, 1931).

More recently the material has been introduced as an antiseptic under the name of Flavine, since changed to Acriflavine (Browning, Gulbransen, Kennaway, and Thornton, Brit. Med. J. 1917, i. 73). Whilst most antiseptics act more powerfully in water than in blood serum, this behaviour is reversed in the case of flavine. Thus flavine kills *Staphylococcus aurens* at a dilution of 1 : 20,000 in water containing 0·7 p.c. of peptone, but at 1 : 200,000 in blood serum. Moreover, flavine has been found to have a low toxicity.

Acridone $C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{CO}{>}C_6H_4$ and its simpler derivatives have no particular interest tinctorially. Anthraquinone-1 : 2-acridone may, however, be dyed from a vat giving reddish-violet shades on cotton (F. Ullmann and P. Ochsner, Annalen, 1911, 381, 9). The substance is obtained by warming *o*-carboxyphenylamino-1-anthraquinone with sulphuric acid.



The necessary carboxylic acid can be obtained from 1-chloroanthraquinone and anthranilic acid or from 1-aminoanthraquinone and *o*-chlorobenzoic acid. The yields are better by the first method, but those by the latter process may be raised to over 90 p.c., especially if in place of *o*-chlorobenzoic acid, its methyl ester be used (Meister, Lucius, and Brüning, D. R. P. 246327; F. Ullmann and P. Dootson, Ber. 1918, 51, 9). On condensing 1-anilino-anthraquinone-2-carboxylic acid a mixture of *o*-carboxyphenylamino-1-anthraquinone and 1-acridineanthraquinone-2-carboxylic acid is obtained (Farbenf. vorm. Fr. Bayer & Co. D. R. P. 262069).

The shades obtained with anthraquinone-acridone are but little altered when chlorine is introduced in position 4 of the anthraquinone nucleus, but the amino- and *p*-toluidino derivatives dye blue and bluish-green respectively (Meister, Lucius, and Brüning, D. R. P. 243586). Ullmann and Dootson have also prepared derivatives substituted in the phenylene nucleus.

The dicarboxylic acid obtained from anthranilic acid and 1 : 5-dichloroanthraquinone may be condensed by sulphuric acid to anthraquinone-1 : 2, 5 : 6-diacridone, which gives a deep blue vat and dyes bluish-violet shades (Ullmann and Ochsner). J. T. H.

ACRIFLAVINE *v. Trypaflavine,* art. ACRIDINE DYESTUFFS.

ACRODEXTRINS *v.* DEXTRINS.

ACROSE *v.* CARBOHYDRATES.

ACTINIUM Ac 230 or 226 (?). A radioactive element, discovered by Debierne in the precipitate produced by adding ammonia and ammonium sulphide to the filtrate from the hydrogen sulphide precipitate obtained in the course of analysing pitchblende (Debierne, Compt. rend, 129, 593; 130, 906). In fractionating the rare earths thus obtained from pitchblende by means of their double nitrates with magnesium nitrate, actinium accumulates in the more soluble portions, together with neodymium and samarium (Compt. rend. 139, 538). The predominating rare earth in pitchblende is thorium; but actinium also occurs in uranium minerals containing no thorium (Szilárd, Chem. Soc. Abstr. 1909, ii. 663). It is a constant constituent of uranium minerals, and is probably derived from uranium in a branch disintegration series.

Actinium has not been isolated nor have its salts been obtained pure. It is similar in chemical properties to the tervalent rare earth elements of the cerium group, and, of these, resembles lanthanum most closely, being more basic (A. von Welsbach, Sitzungsberichte K. Akad. Wiss. Wien, 1910, 119 [iia] 1; Monatsh. 1910, 31, 1150). It is precipitated by oxalic acid, and by ammonia. In presence of ammonium salts the precipitation of actinium is incomplete, but it is completely precipitated in presence of manganese from basic solutions as a manganate. Actinium preparations are highly radioactive, imparting induced radioactivity to surrounding objects (Curie and Debierne, Compt. rend. 132, 548); and, like radium, they spontaneously give rise to helium (Debierne, Compt. rend. 141, 383); they are not luminescent. Their aqueous solutions slowly evolve hydrogen and oxygen in the proportions necessary to form water. Actinium salts also evolve an *emanation*, an inert gas having a molecular weight of approximately 230 (218 or 222 ?), according to diffusion experiments (Debierne, Compt. rend. 136, 446, 767; 138, 411; Bruhat, Compt. rend. 148, 628; Russ, Phil. Mag. 1909, [vi.] 17, 412; Marsden and Wood, Phil. Mag. 1913, [vi.] 26, 948), and condensing to a liquid at −120° to −150° (Kinoshita, Phil. Mag. 1908, [vi.], 16, 121).

The spontaneous decomposition of actinium gives rise to seven successive products: *radio actinium* (Hahn, Ber. 39, 1605; Phil. Mag. 1907, [vi.] 13, 165), which is chemically non-separable from thorium, and which changes into *actinium X*, a substance soluble in ammonia and non-separable from radium (A. Fleck, Trans. Chem. Soc. 1913, 103, 381, and 1052); this transforms into *actinium emanation*, a short-lived gas of the argon family, from which *actinium A*, *actinium B*, *actinium C*, and *actinium D* successively arise (Hahn and Meitner, Chem Soc. Abstr. 1908, ii. 920); they constitute the induced active deposit. The discovery of *actinium A*, an excessively short-lived product, intermediate between the emanation and what previously had been termed *actinium A*, has led to a change of nomenclature, the products previously termed *actinium A*, *B*, and *C* respectively, being now called actinium *B*, *C*, *D* (Rutherford, Phil. Mag. 1911, [vi.] 22, 621). *Actinium B* is chemically non-separable from lead, *actinium C* from bismuth, and *actinium D* from thallium (Fleck, *l.c.*). Actinium itself is rayless; all the other products except *actinium B* and *D* emit α-particles; and *radio-actinium*, *actinium B*, and *actinium D* emit β- rays (Hahn and Meitner, Chem. Soc. Abstr. 1908, ii. 1007; Geiger, Phil. Mag. 1911, [vi.] 22, 201; Geiger and Nuttal, Phil. Mag. 1912, [vi.] 24, 647).

Actinium is identical with the substance *emanium*, discovered by Giesel (*v.* Giesel, Ber. 35, 3608; 36, 342; 37, 1696, 3063; Debierne, Compt. rend. 139, 538; Ann. Phys. 1914 [ix.] 2, 428; Hahn and Sacker, Ber. 38, 1943; *cf.* Marckwald, Ber. 38, 2264; Soddy, Chem. News, 1913, 107, 97).

It occupies the place in the Periodic Table between radium and thorium, and is chemically non-separable from mesothorium-2. Its parent, 'eka-tantalum,' has been separated from pitchblende by distilling the latter in chlorine and carbon tetrachloride vapour at a low red-heat. It probably occupies the place in the Periodic Table between thorium and uranium, and gives actinium in an α-ray change (Soddy and Cranston, Proc. Roy. Soc. 1918. 94, A 384).

Hahn and Meitner (Phys. Zeits. 1918, 19, 208) independently have separated and studied more extensively the parent of actinium. This substance they call 'prot-actinium,' and regard as a higher homologue of tantalum. It emits α-particles of 3·14 cm. range. Its half-value period lies between 1200 and 180,000 years. The growth of actinium from this substance was observed: (1) by means of α-ray curves; (2) by daily measurement of actinium emanation extending over a month; (3) by the active deposit collected in increasing quantities on a negatively charged plate. The observations confirm Curie's value for the half-value period of actinium.

ADALIN. Bromdiethylacetyl urea

$$(C_2H_5)_2CBr{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$$

Used as a hypnotic.

ADAMANTINE SPAR *v.* Corundrum

ADAMITE. A mineral consisting of hydrated basic zinc arsenate $Zn_3(AsO_4)_2{\cdot}Zn(OH)_2$, discovered by C. Friedel in 1866 as a few small, violet orthorhombic crystals on silver ores from Chañarcillo in Chile. Since then it has been found at a few other localities, particularly in the ancient zinc mines at Laurion in Greece. Here it occurs in some abundance as bright green (cupriferous) or yellowish crystals in cavities of the cellular zinc ores. It has been prepared artificially in a crystalline condition.

More recently the name *adamite* has been employed as a trade name for an artificial corundum manufactured for abrasive purposes.

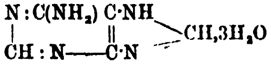
L. J. S.

ADAMON. Trade name for dibromodihydrocinnamic acid bornyl ester.

ADANSONIA DIGITATA (Linn.), the *Baobab tree*, yields a fibre which has been used in paper-making. Its bark (Gowik Chentz or Churre Chentz) is said by Duchaissaing to be a useful substitute for cinchona (Dymock, Pharm. J. [3] 7, 3).

ADENASE *v.* ENZYMES.

ADENINE, 6-*Aminopurine*



$$\begin{array}{l} N:C(NH_2)\,C{\cdot}NH \\ |\qquad\qquad\;\; \| \qquad\quad \searrow CH,3H_2O \\ CH:N\text{——}C{\cdot}N \;\nearrow \end{array}$$

discovered in the pancreatic gland and spleen of the ox, occurs in all vegetable and animal tissues rich in cells (Kossel, Ber. 1885, 18, 79, 1928; Zeitsch. physiol. Chem. 1886, 10, 248; Yoshimura and Kania, Zeitsch. physiol Chem. 1913, 88, 351; Minuroto, J. Coll. Agric. Imp. Univers. Tokio, 1912, 5, 63; Smorodinzew, Zeitsch. physiol. Chem. 1912, 80, 218; Zlataroff, Zeitsch. Nahr. Genussm. 1913, 26, 242; Bass, Arch. f. exp. Pathol. u. Pharmak. 76, 40–64; Winterstein, Landw. Vers.-Stat. 79 and 80, 541–562; Chapman, Chem. Soc. Trans. 1914, 105, 1903-1904); thus it has been extracted from tea leaves (Kossel, *l.c.*), from beet-juice (v. Lippmann, Ber. 1896, 29, 2645), from beet-sugar residues (Andrlík, Zeitsch. Zuckerind, Bohm. 1910, 34, 567–569), 0·05 p.c. pure adenine obtained, from molasses (Stoltzenberg, Chem. Zentr. 1912, 1515, from Zeitsch. ver deut. Zuckerind, 1912, 318), from the young shoots of bamboo (Totani, Zeitsch. physiol Chem. 1909, 62, 113); from human excretory products (Kürger and Schittenhelm, Zeitsch. physiol. Chem. 1902, 35, 159), and from herring brine (Isaac, Chem. Zentr. 1904, ii. 647; from Beitr. chem. physiol. Path. 1904, 5, 500); it is probably one of the degradation products of nucleïn (Schindler, Zeitsch. physiol. Chem. 1889, 13, 432), and is found in small quantity when nucleïn is heated with dilute sulphuric acid (Kossel, Ber. 1885, 18, 1928; Jones and Richards, J. Biol. Chem. 1914, 17, 71; 1915, 20, 25–35).

It has been obtained from rice polishings (Drummond and Funk, Bio-chem. J. 1914, 8, 598-615), and, according to Funk, is of distinct therapeutic value (Casimir Funk, J. Physiol. 1913, 45, 489; also J. Biol. Chem. 1916, 26, 431–456; and Harden and Zilva, Biochem. J. 1917, ii. 172).

Adenine is isolated from tea extract after the removal of caffeine by precipitating the cuprous compound $C_5H_3N_5Cu_2$ by means of copper sulphate and sodium bisulphite, and decomposing the precipitate with ammonium sulphide; the crude adenine is then isolated from the filtrate in the form of the sulphate. For the method of separating adenine from other purine bases compare Schindler (Zeitsch. physiol. Chem. 1889, 13, 432). For recovery of adenine from the picrate, *see* Barnett and Jones (J. Biol. Chem. 1911, 9, 93–96). The synthesis of adenine has been effected by reducing with hydriodic acid 2-amino-2 : 8-dichloropurine obtained by the action of aqueous ammonia on trichloropurine (E. Fischer, Ber. 1897, 30, 2226; 1898, 31, 104; Böhringer and Sons, D. R. P. 96927, 24/3, 97; Traube, Annalen, 1904, 331, 64).

Adenine crystallises from dilute aqueous solution in long rhombic needles that become anhydrous at 110°, and melt with decomposition when rapidly heated at 360°–365° (Fischer, *l.c.*), and sublime in microscopic needles without decomposition at 220°. Adenine is sparingly soluble in cold (1 : 1086) and readily soluble in hot water (1 : 40); sparingly so in alcohol; insoluble in ether or chloroform. It forms compounds with bases, acids, and salts; with hexose (Maudel and Dunham, Biochem. J. 1912, xi. 85), and gives mono- and dichloro-glucosides (Fischer and Helferich, Ber. 1914, 47, 210–235). Adenine *d*-glucoside has m.p. 210°-275° (decomposed), $[\alpha]_D$ 19°–20° $-10{\cdot}5°$ in water, $+5{\cdot}67°$ in *N*/hydrochloric acid. The *nitrate*

$$C_5H_5N_5,HNO_3,\tfrac{1}{2}H_2O$$

is crystalline, and the dry salt dissolves in 110·6 parts of water; the *hydrochloride*

$$C_5H_5N_5,HCl,\tfrac{1}{2}H_2O$$

forms transparent monoclinic prisms $a : b : c = 2{\cdot}0794 : 1 : 1{\cdot}8127$, $\beta = 61°\ 40'$ the anhydrous salt dissolves in 41·9 parts of water; the *chloracetate* $C_5H_5N_5,C_2H_3O_2Cl$ melts and decomposes at 162°–163°; the *sulphate*

$$(C_5H_5N_5)_2,H_2SO_4,2H_2O,$$

the *oxalate* $C_5H_5N_5,C_2H_2O_4,H_2O$, and *dichromate* $(C_5H_5N_5)_2,H_2Cr_2O_7$ are crystalline; the *picrate* $C_5H_5N_5,C_6H_3N_3O_7$ is stable at 220°, and is so sparingly soluble in cold water (1 : 3500) that it is used as a means of estimating adenine in solution (Ber. 1890, 23, 225); the addition of sodium picrate will precipitate adenine from exceedingly dilute solutions (1 : 13,000) (Barnett and Jones, J. Biol. Chem. *l.c.*); the *picrolonate* $C_5H_5N_5,C_{10}H_8O_5N_4$ crystallises from water and melts at 265° (Levene, Biochem. Zeitsch. 1907, 4, 320). The *platinichloride* $(C_5H_5N_5)_2,H_2PtCl_6$ crystallises from dilute solution in needles, and yields the *salt* $C_5H_5N_5,HCl,PtCl_4$ when a concentrated solution is boiled. The *acetyl* derivative $C_5H_4N_5Ac$ does not melt at 260°, the *benzoyl* derivative $C_5H_4N_5Bz$ has m.p. 234°–235° (Kossel, Ber. 1886, 20, 3356). The *methyl* and *benzyl* derivatives have been prepared (Thoiss, Zeitsch. physiol. Chem. 13, 395). *Bromadenine* $C_5H_4N_5Br$ is strongly basic, forms an insoluble *picrate*, and on oxidation with hydrochloric acid and potassium chlorate yields alloxan, urea, and oxalic acid (Bruhns, Ber. 1890, 23, 225; Krüger, Zeitsch. physiol. Chem. 1892, 16, 329). Adenine is converted into hypoxanthine by the action of nitrous acid (Kossel, Ber. 1885, 18, 1928). Adenine-*d*-glucoside treated with excess of nitrous acid yields hypoxanthine-*d*-glucoside, m.p. 245°, $[\alpha]_D^{20°}$ −34·5° in *N*/soda, +12·92° in *N*/hydrochloric acid (Fischer and Helferich, *l.c.*).

Adenine-uracil-dinucleotide is obtained as an amorphous powder by the action of dilute ammonium hydroxide on yeast-nucleic acid; it has $[\alpha]_D$ −6·8°, and gives a crystalline brucine salt $C_{19}H_{25}O_{15}N_7P_2,4C_{23}H_{26}O_4N_2,14H_2O$, m.p. 174°–175° (decomp.). M. A. W.

ADHESIVES, as distinguished from cements, may be defined to be substances or preparations of a gummy or gelatinous character used for the purpose of joining together or effecting the mutual adhesion of the surfaces of bodies. They are usually substances which (1) soften in water, *e.g.* gum arabic, isinglass, glue, &c.; (2) gelatinise in water or other menstruum, and harden either by the evaporation of the solvent or its absorption by the cohering surfaces, *e.g.* liquid glue, gelatine dissolved in acetic acid, rubber or guttapercha in benzene, &c.; or (3) which soften on heating and congeal on cooling, *e.g.* asphalt, marine glue, shellac, &c. The surfaces of the articles to be joined should be perfectly clean; they should be brought into intimate contact, and as little of the adhesive as possible employed. In certain cases perfect contact is ensured by heating the parts to be joined to a temperature such that the adhesive solidifies only when union is effected.

Solutions of gum arabic, or of dextrin, or British gum, mixed with acetic acid, are frequently employed in the case of paper. Flour or starch mixed with water containing a little alum so as to form a thick cream, which is then heated to boiling, and when cold mixed with oil of cloves, thymol, phenol, or salicylic acid so as to preserve it, makes an effective adhesive. A transparent paste may be made by the use of rice starch instead of ordinary flour. Occasionally a small quantity of linseed oil or glycerol is added in the case of labels exposed to moisture. Or the labels may be protected from damp by being coated with a mixture of 2 pts. shellac, 1 pt. borax, dissolved in 16 pts. of boiling water. An alternative method is to apply a coating of copal varnish.

A strong adhesive may be made from shredded gelatine, swollen in water containing 25 p.c. of glacial acetic acid and applied hot. The mixture should be kept in a closely corked phial. Another recipe: Dissolve 60 pts. borax in 420 pts. water, add 480 pts. dextrin and 50 pts. glucose, and heat carefully—not above 90°—with constant stirring until the whole is in solution; replace the evaporated water and filter through flannel (Hiscox).

Wheat flour rich in proteins is mixed with concentrated sulphite liquors and evaporated to a suitable consistency (Robeson). Flour and molasses mixed to a stiff paste or stiff flour paste and concentrated zinc chloride make a permanent cement. Dry casein mixed with half its weight of borax and a sufficiency of water makes an excellent adhesive for broken china or earthenware. Finely powdered casein 12 pts., fresh slaked lime 50 pts., fine sand 50 pts., and enough water to make a thick mass makes a strong cement for ground unions standing a moderate heat. Milk casein dissolved in alkali and an alkaline silicate, such as water-glass, and mixed with a solution of magnesium or calcium chloride, also constitutes an effective adhesive. White of egg made into a paste with slaked lime used immediately after being made up is a very tough and tenacious adhesive. Linseed oil mixed with china clay, or lime, or red or white lead, or oxide of iron, to which powdered glass or graphite may be added adheres strongly when set.

Metallic surfaces after having been rubbed with an alcoholic solution of hydrochloric acid may be caused to adhere by means of a mixture of 10 pts. tragacanth mucilage, 10 pts. honey, and 1 pt. flour (Spon).

A *marine glue* may be used by dissolving 10 pts. caoutchouc in 120 pts. benzene, and adding the solution to 20 pts. melted asphaltum, the mixture being poured into moulds to consolidate. In order to use it the glue is soaked in boiling water and heated over a flame until liquid.

As a leather cement: asphalt, 1 pt.; rosin, 1 pt.; gutta-percha, 4 pts.; carbon disulphide, 20 pts. A plain rubber cement is made by dissolving crude rubber in carbon disulphide or benzene.

Good waterproofing cements are: (1) rosin, 1 pt.; wax, 1 pt.; powdered stone, 2 pts. (2) Shellac, 5 pts.; wax, 1 pt.; turpentine, 1 pt.; chalk, 8–10 pts. For a soft air-tight paste for ground glass surfaces: a mixture of equal parts of wax and vaseline. A solution of 1 pt. of powdered shellac in 10 pts. of ammonia water makes a strong cement for porcelain, glass, and metals (not copper).

Plastic cements, as distinguished from adhesives of the foregoing nature, are used in chemical industry to secure joints and make connections of a more or less temporary character. Such are plaster of Paris used either alone or mixed with asbestos; or when a high temperature is not required, mixed with shavings, straw, hair, cloth, &c. Hydraulic cement used alone or mixed with asbestos or sand, is used as a lute; it is especially resistant to acid vapours. Ordinary clay or fire clay mixed with linseed oil is often employed for steam-joints. A mixture of fire clay, 2 pts.; sulphur, 1 pt.; rosin, 1 pt., may be used for nitric and hydrochloric acid vapours. Mixtures of (1) pitch, 8 pts.; rosin, 6 pts.; wax, 1 pt.; plaster, ¼–½ pt.; or (2) pitch, 8 pts.; rosin, 7 pts.; sulphur, 2 pts.; stone powder, 1 pt., may be used to unite slate slabs and stoneware for engineering and chemical purposes. *See* LUTES.

ADIGAN. A preparation of digitalis (*q.v.*).

ADIPIC ACID *Butane-α-δ-dicarboxylic acid* $CO_2H{\cdot}(CH_2)_4{\cdot}CO_2H$. Obtained by the action of nitric acid on sebacic acid, or on tallow, suet, and other fatty bodies (Arppe, Z. 1865, 300; Laurent, Ann. Chim. Phys. [2] 66, 166; Bromeis, Annalen, 35, 105; Malaguti, Ber. 1879, 572). It is present in beet-juice (Lippmann, Ber. 1891, 3299), and may be obtained from Russian petroleum by distilling the fraction containing naphthalene hydrocarbons (Aschan, Ber. 1899, 1769). It may be prepared by the reduction of mucic acid (Crum-Brown, Annalen, 125, 19), saccharic acid (de la Motte, Ber. 1879, 1572), *iso*saccharic acid with hydriodic acid and phosphorus, or of muconic acid with sodium amalgam (Marquardt, Ber. 1869, 385); by heating β-iodopropionic acid with silver (Wislicenus, Annalen, 149, 221); by the electrolysis of the potassium salt of the monoethyl ester of succinic acid, whereby the diethyl ester of adipic acid is produced (Brown and Walker, Annalen, 261, 117); by oxidising cyclo-hexanone with potassium permanganate in the presence of sodium carbonate (Rosenlew, Ber. 1906, 2202; Mannich and Hancu, Ber. 1908, 575).

Adipic acid crystallises in monoclinic laminæ, melts at 149°, and sublimes at a still higher temperature (Wirz, Annalen, 104, 257). *Cyclo*-pentanone is produced when the calcium salt is distilled, and no anhydride is obtained by the distillation of the acid. It is slightly soluble in water at the ordinary temperature, and has a great tendency to form supersaturated solutions (Dieterle and Hell, Ber. 17, 2221); readily soluble in hot alcohol and ether. It forms salts with most metals which are generally soluble in water and crystallisable. There are eight isomerides of adipic acid, all of which have been prepared.

ADIPOCERE (from *adeps*, fat; and *cera*, wax). A peculiar waxy-looking substance, first observed by Fourcroy in 1786, when the bodies were removed from the *Cimetière des Innocents* at Paris. A large number of coffins had been piled together and had so remained for many years; the corpses in many of these were converted into a saponaceous white substance. Fourcroy placed this substance, together with cholesterol and spermaceti, in a separate class termed by him 'Adipocere.' Gregory (Annalen, 1847, 61, 362), observed a similar substance in the case of a hog which had died of an illness, and had been buried on the slope of a mountain-side. The substance was completely soluble in alcohol, contained no glycerides, and consisted, according to Gregory, of about 25 p.c. of stearic acid, and about 75 p.c. of palmitic and oleic acids (these three acids form the chief constituents of lard). The absence of lime was explained by Gregory as due to the solvent action of water saturated with carbonic acid, which continually ran over the carcase. Gregory fully recognised that the fatty acids had been formed by the hydrolysis of the fat, water having washed away all the glycerol simultaneously produced, and he clearly stated his view that from corpses of animals all nitrogenous and earthy constituents could be washed away, fatty acids only remaining behind. Ebert (Ber. 8, 775) in the main confirmed these results in the examination of a specimen of adipocere. On saponifying with potash, about 1 p.c. ammonia escaped and an insoluble residue (about 6 p.c.), consisting of lime, &c., from tissues, remained. A mixture of potassium salts was obtained, which by fractional precipitation with magnesium acetate yielded mainly palmitic acid. The last fraction, not precipitable by magnesium acetate, but by lead acetate, yielded a hydroxylated acid, the formula of which is given as $C_{17}H_{34}O_3$. This acid, termed by Ebert hydroxymargaric acid, melts at 80°, and is most likely 1 : 10 hydroxystearic acid of the melting-point 81°. The occurrence of this acid in the adipocere examined by Ebert is very likely, as he could not detect any oleic acid; it would thus appear that in the course of time the oleic acid had been oxidised to 1 : 10 hydroxystearic acid. The hard waxy character of adipocere is mainly due to the presence of hydroxystearic acid. Schmelck (Chem. Zeit. 1902, 11) found in the examination of three specimens of adipocere the following results :—

Melting-point . . .	62·5° C.
Insoluble fatty acids .	83 84 p.c.
Ash	1·7 p.c. (containing 83·5 p.c. CaO)
Unsaponifiable matter	16·7 p.c.
Acid value	197
Neutralisation value of the fatty acids . .	203
Iodine value . . .	14

Tarugi (Gazz. chim. ital. 34, ii. 469) also states that adipocere consists chiefly of palmitic acid.

According to Ruttan (Trans. Roy. Soc. Canada, 1917 [iii.] 10, 169) the two isomeric monohydroxystearic acids derived from oleic acid are invariably present, and the disappearance of oleic acid marks the final change in the formation of mature adipocere (*cf.* Ruttan and Marshall, Proc. Amer. Soc. Biol. Chem. 1915).

The formation of adipocere from animal matter had been studied by Kratter in glass vessels filled with water. Kratter's opinion that adipocere originates from the albuminoids must, however, be rejected as erroneous, for there can be no doubt but that the free fatty acids are formed by the hydrolysis of the body fat. All the decomposition products of the albuminoids and the glycerol would be washed away, and the fatty acids would naturally form with the lime of the bones, lime soaps, which may or may not be further hydrolysed by water, to free acid and lime, according to the conditions obtaining in the decomposition of the body. Bacterial and enzymic actions play a quite secondary part in the production of adipocere.

J. L.

ADLUMINE $C_{39}H_{41}O_{12}N$, crystals, m.p. 188°, occurs in *Adlumia cirrhosa* (Rafin.) with *adlumidine* $C_{30}H_{29}O_9N$, plates, m.p. 234°, protopine, and β-homochelidonine (Schlotterbeck and Watkins, Ph. Ar. 1903, 6, 17).

ADONIDIN. A digitalis-like glucoside said to be extracted from the root of *Adonis vernalis* or false hellebore. *v.* DIGITALIS.

ADONITOL. *See* CARBOHYDRATES.

ADORIN. Trade name for a mixture of some powder (infusorial earth, starch, &c.) with paraformaldehyde. Used as a wound dressing.

ADRENALINE. *Adrenalinum B.P.*, *Epinephrine*, *Suprarenin*

$$C_6H_3(OH)_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NH{\cdot}CH_3$$

The U.S.P. has dried suprarenal gland, *Suprarenalum siccum*, but not the active principle. A 'chromogen,' coloured green by ferric chloride and rose-red by iodine, was discovered in the suprarenal medulla by Vulpian (Compt. rend. 1856, 43, 663), but the remarkable rise of blood pressure caused by intravenous injection of suprarenal gland extracts was not observed until 1894 (Oliver and Schäfer, J. Physiol. 1894, 16, i.). After numerous attempts the active principle, which turned out to be also the chromogen, was first obtained crystalline by Takamine (Eng. Pat. 1467, 1901; J. Soc. Chem. Ind. 20, 746), and almost simultaneously by Aldrich (Amer. J. Physiol. 1901, 5, 457). The constitution was next established, mainly by Pauly (Ber. 1903, 36, 2944; 1904, 37, 1388) and by Jowett (Trans. Chem. Soc. 1904, 85, 192). The racemic substance was synthesised by Stolz (Ber. 1904, 37, 4149; and D. R. P. 152814, 157300 of Farbw. Meister, Lucius und Brüning; *cf.* also Dakin, Proc. Roy. Soc., B. 1905, 76, 491). As the racemic substance was found to have little more than half the activity of the natural lævo-variety, its resolution was effected by Flacher (Zeitsch. physiol. Chem. 1908, 58, 581; and D. R. P. 222451 of Farbw. Meister, Lucius und Brüning). The synthetic *l*-base thus obtained is identical with the natural active principle, and is known commercially as *suprarenin.*

The name *epinephrine* was first applied by Abel to *N*-benzoyl adrenaline, but later to the active substance itself, and it is under this name that the substance is referred to in the U.S.P., for instance. The objection to adrenaline is that it is a trade name; close on thirty other trade names have been in use for the substance.

Preparation of natural substance.—The minced glands (generally of oxen) are extracted with acidulated water at 90°–100°; the extract is evaporated to a small bulk, it may then be purified with neutral lead acetate, and it is finally precipitated with several volumes of ethyl or methyl alcohol. The alcoholic filtrate, after concentration to a small bulk, is precipitated with excess of *concentrated* ammonia, when the adrenaline crystallises in sphaerites on standing. Oxidation must be guarded against as far as possible, by boiling with zinc dust, or by extracting with water containing sulphur dioxide; the evaporation is conducted *in vacuo* in a carbon dioxide atmosphere and the precipitation by ammonia takes place under a layer of petrol (Takamine, *l.c.*; Aldrich, *l.c.*; von Fürth, Monatsh. 1903, 24, 261). Abel (Ber. 1903, 36, 1839) extracts at once with a 3·5 p.c. alcoholic solution of trichloracetic acid, which eliminates further purification, and seems to give a good yield. Bertrand (Bull. Soc. chim. 1904, [iii.] 31, 1289) extracts with 95 p.c. alcohol containing oxalic acid, evaporates, shakes with petrol, and purifies with lead acetate.

The crude sandy adrenaline contains inorganic matter, and may be purified by solution in acid and reprecipitation, but better by utilising the solubility of the oxalate in alcohol; the crude base is ground up with a 15 p.c. solution of oxalic acid in 85–90 p.c. alcohol, which leaves inorganic impurities behind (Abel, Pauly).

Syntheses.—Catechol is condensed with monochloracetic acid, by means of phosphorus oxychloride, and the resulting chloracetocatechol (3 : 4-dihydroxy-ω-chloracetophenone)

$$\mathrm{(OH)_2C_6H_3{\cdot}CO{\cdot}CH_2Cl}$$

is suspended in alcohol (50 c.c. for 100 grams. of the ketone); 200 c.c. of a 40 p.c. aqueous methylamine solution are added; on standing methylaminoacetocatechol

$$\mathrm{(OH)_2C_6H_3{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}CH_3}$$

separates out, and is washed with water, alcohol, and ether. The ketone is then reduced to the secondary alcohol by aluminium amalgam, or electrolytically. For the resolution the bitartrate is extracted with methyl alcohol; *d*-adrenaline-*d*-tartrate dissolves and *l*-adrenaline-*d*-tartrate remains behind. The *d*-adrenaline so obtained is also utilised, for it may be racemised by heating with dilute hydrochloric acid, and converted into the crystalline racemic hydrochloride (D. R. P. 220355), which can then again be resolved.

The synthesis from chloracetocatechol appears to be the only one of practical importance, but various others have been described. The methylene ether of adrenaline was synthesised by Barger and Jowett (Trans. Chem. Soc. 1905, 87, 967) from piperonal, but could not be hydrolysed to adrenaline, and other attempts in this direction were also unsuccessful (*cf.* Pauly and Neukam, Ber. 1908, 41, 4151; Barger, Trans. Chem. Soc. 1908, 93, 2081; Böttcher, Ber. 1909, 42, 253; Pauly, *ibid.* 1909, 42, 484; Mannich, Arch. Pharm. 1910, 248, 127; D. R. P. 209609, 209610, 212206). Another adrenaline synthesis referred to in the patent literature, consists in methylating the primary base corresponding to adrenaline, namely 3 : 4-dihydroxyphenylethanolamine. This substance, known commercially as *arterenol,* may be obtained (*a*) by the reduction of amino-acetocatechol (D. R. P. 155632); and (*b*) by the reduction of the cyanhydrin of protocatechuic-aldehyde with sodium amalgam (D. R. P. 193634). The latter reaction may be represented thus:

$$\mathrm{(OH)_2C_6H_3{\cdot}CH(OH){\cdot}CN+4H}$$
$$\mathrm{=(OH)_2C_6H_3{\cdot}CH(OH){\cdot}CH_2NH_2}$$

Amino-acetocatechol may be produced (*a*) from chloracetocatechol (above); (*b*) from piperonal or methyl vanillin, *via* ω-nitroacetocatechol, which is reduced (D. R. P. 195814) thus:

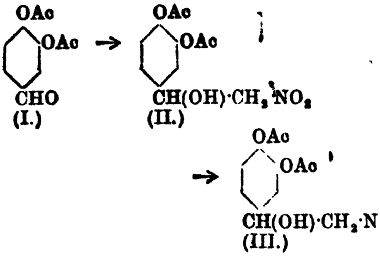
$$\mathrm{(OH)_2C_6H_3{\cdot}CO{\cdot}CH_2{\cdot}NO_2+6H}$$
$$\mathrm{=(OH)_2C_6H_3{\cdot}CO{\cdot}CH_2{\cdot}NH_2}$$

(*c*) by hydrolysis of the condensation products of veratrole with hippuryl chloride (D. R. P. 185598 and 189483)

$$\mathrm{(MeO)_2C_6H_3{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}C_6H_5}$$
$$\rightarrow \mathrm{(OH)_2C_6H_3{\cdot}CO{\cdot}CH_2{\cdot}NH_2}$$

or by hydrolysis of the similarly constituted phthalimido-acetoveratrole (D. R. P. 209962 and 216640). The last-mentioned four patents are of Farbenfabriken vorm. F. Bayer & Co., all the others of Farbw. vorm. Meister, Lucius und Brüning (*cf.* Friedländer, viii. 1181–1190; ix. 1024–1033). The most recent synthesis is a modification of some earlier ones.

Diacetylprotocatechuic aldehyde I, on condensation with nitromethane in feebly alkaline aqueous solution yields β-hydroxy-β-3 : 4-diacetoxyphenylnitroethane (II.). When this is mixed with the calculated quantity of formaldehyde and reduced by zinc and acetic acid, β-hydroxy-β-3 : 4-diacetoxyphenyl ethyl methylamine (III.) is formed, from which adrenaline is obtained on removal of the acetyl groups :—



(N. Nagai, Jap. Pats. 32440, 32441, 1918).

Properties.—Natural adrenaline, when pure, forms colourless sphaero-crystals, m.p. 211°-212°, $[\alpha]_D - 53°$; the solubility in water at 20° is 0·0268 p.c., and it is also very slight in most organic solvents. Racemic adrenaline decomposes at 230°. Adrenaline dissolves in the calculated quantity of mineral acids, or even in slightly less; it also dissolves in caustic alkalis. Its chief chemical characteristic is the ease with which it undergoes oxidation (*see* colour reactions, below). Solutions with a slight excess of acid are the most stable; traces of iron accelerate oxidation (Gunn and Harrison, Pharm. J. 1908, [iv], 26, 513).

The salts of the optically active adrenalines are mostly amorphous and deliquescent; the *borate* is said to be more stable (D. R. P. 167317). The chief crystalline salt is the *bitartrate* employed in the resolution of the racemic base. The latter yields a crystalline *hydrochloride*, m.p. 157° (D. R. P. 202169), and a crystalline *oxalate*; the corresponding optically active salts are amorphous.

Colour reactions. Colorimetric estimation.—There are three kinds of colour reactions for adrenaline: (1) the general catechol reaction with ferric chloride (limit of green coloration 1 : 30,000); (2) the phosphotungstic reaction of Folin, Cannon and Denis (Journ. biol. Chem. 1913, 13, 477; *cf.* Folin and Denis, *ibid.* 1912, 12, 239), in which the reagent gives a highly coloured blue reduction product; (3) a reaction with a considerable number of mild oxidising reagents, in which the adrenaline is converted into apparently one and the same rose-red oxidation product. For the colorimetric estimation of pure adrenaline solutions the reaction of Folin, Cannon and Denis is the most suitable, and agrees closely with physiological measurements (Seidell, Journ. biol. Chem. 1913, 15, 197; Johannessohn, Biochem. Zeitschr. 1916, 76, 377). The reagent employed is the same as for the estimation of uric acid, but adrenaline is three times as sensitive (Johannessohn gives the ratio 2–98). 100 grams sodium tungstate are dissolved in 750 c.c. of water, and after adding 80 c.c. of 85 p.c. (syrupy) phosphoric acid, the solution is boiled gently for $1\frac{1}{2}$–2 hours, and then made up to 1 litre; $\frac{1}{300}$–$\frac{1}{400}$ mg. adrenaline can be detected; limit 1 : 3,000,000. The blue colour soon fades. Uric acid solutions are used as standards.

For the estimation of adrenaline in extracts of the gland which are always more or less yellow in colour, the phosphotungstate reagent is less suitable (Seidell, *l.c.*), and it is unsuitable for mixtures of adrenaline with cocaine, novocaine, &c., because the latter bases are precipitated by the reagent (Johannessohn, *l.c.*). In these cases a reaction of the third type seems preferable (3). Seidell shakes 10 c.c. of gland extracts containing 1 : 50,000 adrenaline, for one hour with 5 mg. of powdered manganese dioxide, filters, and matches the colour with that of standards, prepared by mixing, in various proportions, a solution of 2 grams $CoCl_2 \cdot 6H_2O + 1$ c.c. concentrated hydrochloric acid in 100 c.c. water, with an auric chloride solution containing 0·1 gram $AuCl_3$ in 100 c.c. water. These mixtures are standardised by comparison with a 1 : 100,000 solution of pure adrenaline, mixed with an extract of desiccated thyroid gland (which has the same yellow colour as a suprarenal extract).

For mixtures containing cocaine, &c., Johannessohn employs the Fränkel-Allers reaction (Biochem. Zeitsch. 1909, 18, 40), which consists in adding an equal volume of 0·001 *N*-potassium *bi*-iodate and a few drops of phosphoric acid, and heating nearly to the boiling-point; a red colour is obtained with adrenaline up to 1 : 100,000 or 1 : 300,000. Other oxidising reagents giving a red colour are auric chloride (Gautier, Compt. rend. Soc. de Biol. 1912, 73, 564; very delicate), potassium persulphate (Ewins, J. Physiol. 1910, 40, 317; 1 : 5,000,000), iodine, mercuric chloride, potassium ferricyanide, bromine, bleaching powder, osmic acid. For a detailed criticism of the quantitative application of these reagents, *see* Borberg (Skand. Arch. Physiol. 1912, 27, 341), also Bayer (Biochem. Zeitsch. 1909, 20, 178) for means of making them more sensitive but less specific.

Physiological methods of estimating adrenaline are more reliable, and may be more accurate than the colorimetric ones. The blood pressure of a cat, with brain and spinal cord destroyed, and without anæsthetic, reacts, according to Elliott (J. Physiol. 1912, 44, 374), 'with mechanical accuracy,' and permits of the estimation of the adrenaline content of a cat's supra-renal with an error of 0·01 mg. (3-4 p.c. of the total amount present). Moderately accurate results may also be obtained with frogs (Läwen, Arch. exp. Path. Pharm. 1904, 51, 415; Trendelenburg, *ibid.* 1910, 63, 161).

Fresh bullock's supra-renals may contain up to 0·25 p.c. adrenaline; the desiccated gland (U.S.P.), corresponding to 6 pts. of the fresh gland, may contain about 1·5 p.c. A fresh bullock's gland dissected free from fat weighs about 10–12 grams. The actual yield in manufacture often does not exceed 0·1 p.c. from bullock's glands; sheep, and especially hogs, contain less. The dried secretion of the parotid gland of *Bufo agua*, a Central American toad, contains as much as 5 p.c. of adrenaline (Abel and Macht, J. Pharm. exp. Ther. 1912, 3, 319).

The most important *physiological action* of adrenaline is that on the arterioles, causing constriction and rise of blood pressure. Intravenously minute doses (0·0003 mg. per kilo in rabbits) produce a distinct effect. Applied to a mucous surface, it causes marked local vaso-constriction and blanching; on this property depends its chief use as a hæmostatic in surgery. It is often used mixed with a local anæsthetic like cocaine. Most commercial solutions and the *Liquor adrenalini hydrochloricus* of the B.P. contain 0·1 p.c. adrenaline dissolved in a slight excess of acid (*e.g.* one-half equivalent) which renders them more stable than solid tablets (according to Johannessohn, *l.c.*; Gunn and Harrison, *l.c.*). Chloroform (B.P.) or other preservative may be added, and salt to make the solution isotonic with the blood. For sterilisation by heat, *see* Rowe (Amer. J. Pharm. 1914, 86, 145). Adrenaline has been recommended (in oral doses of 5–6 mg. per 24 hours) for sea-sickness (Revue Scientifique, 1917). The physiological activity of *d*-adrenaline is about $\frac{1}{15}$ of that of *l*-adrenaline (*e.g.* Cushny, J. Physiol. 1909, 38, 259; Tiffeneau, Compt. rend. 1915, 161, 36), and hence the racemic base is slightly more than half as active as the natural variety.

Adrenaline Substitutes.—Numerous amines have an action more or less resembling that of adrenaline (Barger and Dale, J. Physiol. 1910, 41, 19). Three, all closely related to adrenaline in structure, have been recommended as substitutes, but have not found wide application. Racemic 'arterenol,' 3 : 4-dihydroxyphenylethanolamine $(OH)_2C_6H_3{\cdot}CH(OH){\cdot}CH_2.NH_2$ (*see* above), m.p. 191° (hydrochloride, m.p. 141°), is said to be about half as active as *l*-adrenaline. *Homorenon*, ω-ethylamino-3 : 4 dihydroxyacetophenone $(OH)_2C_6H_3{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}C_2H_5$ has a crystalline hydrochloride, m.p. 260°, and a very much weaker action than adrenaline. *Epinine*, 3 : 4-dihydroxyphenylethylmethylamine $(OH)_2C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_3$, m.p. 188°–189° (Pyman, Trans. Chem. Soc. 1910, 97, 272), is intermediate in action between the two former bases. (For Tyramine, *see* article on ERGOT.)

For a more detailed account of the chemical and physiological properties of adrenaline, *see* Barger, The Simpler Natural Bases, Longmans, 1914, pp. 81–105. G. B.

ADRENCAINE. *See* EUDRENINE.

ADSORPTION *v.* COLLOIDS.

ADUROL. Trade name for a haloid substitution product of hydroquinone, used as a photographic developer.

AËRATED or MINERAL WATERS.

Originally the term 'mineral water' was used to describe natural spring waters containing small quantities of various salts in solution, and frequently saturated with carbon dioxide, hydrogen sulphide, or other gases. When these waters were first imitated by the artificial introduction of carbon dioxide into dilute saline liquids, they were known as 'aërated waters,' to distinguish them from the natural products. At the present time the two terms are employed indiscriminately, and as a rule the whole of the products of the manufacturer of aërated waters are popularly known as 'mineral waters.'

Natural Mineral Waters. In every quarter of the globe natural spring waters containing salts with medicinal properties are common, though fashion has made some more celebrated than others. Some of these waters (*e.g.* Hunyadi Janos) contain magnesium and sodium sulphate, and have an aperient action, whilst others containing iron (*e.g.* Tunbridge Wells water) are valued as tonics. Others, again, like the waters of Harrogate, contain sodium sulphide (0·02 p.c.), and are used as remedies in various complaints.

The most widely consumed natural mineral waters are those which contain only a small proportion of salts and a large amount of carbon dioxide. Typical examples of these are Apollinaris water, Selters water, and St. Gaulmier (French).

The table of analyses (p. 50) show the chief constituents of typical natural mineral waters.

Small quantities of many other compounds are also present in all these waters, but the figures given above represent their main constituents. The composition of all natural mineral waters varies from time to time, but they preserve their general characteristics.

Artificial Mineral Waters. Special mixtures of salts approximately corresponding in composition to those in many of the well-known medicinal waters are now sold, with directions for preparing solutions, which, when aërated, shall produce passable imitations of the natural products.

Among the purely artificial mineral waters mention must be made of ***seltzer water***, which is prepared somewhat upon the lines of the natural Selters water, and contains sodium carbonate, chloride, and sulphate, and sometimes calcium and magnesium chlorides, the proportion of these ingredients being varied to suit the popular taste of the district. It is bottled at a pressure of about 120 lbs., corresponding to about 45–55 lbs. in the bottle.

Other medicinal artificial mineral waters include soda-water, potash-water, lithia-water, and magnesia-water. Soda-water was an official drug in the London Pharmacopœia of 1836, but was not introduced into the British Pharmacopœia until 1867. In the present Pharmacopœia (1898) it is omitted, together with the other alkaline waters. There is thus now no standard for soda-water, and since the old standard of 30 grains of sodium bicarbonate to the pint is sometimes found too alkaline to be palatable, a large proportion of the soda water upon the market contains much less than the old specified proportion of alkali.

Methods of Aërating.—The process of impregnating water with carbon dioxide under pressure dates back to the middle of the 18th century, one of the earliest inventors of apparatus for the purpose being the Duke de Chaulnes in France. In this country the artificial 'aëration' of water was suggested by Bewley in 1767, and in 1772 Priestley constructed an apparatus somewhat on the principle of the modern Kipps' gas generator. A similar apparatus was devised about the same time by Bergman, and was extensively used throughout Sweden.

The earliest processes of bottling aërated waters made use of what is known as the 'Geneva' or ***semi-continuous*** process, in which the carbon dioxide, after being generated from chalk and acid, was forced under pressure with water into a cylinder, whence it could be drawn off into the bottles. This process, which is still employed in modified forms, is useful when a relatively small amount of liquid is to be impregnated, but has the drawbacks of requiring the work to be interrupted to recharge the cylinder, and of bottling the liquid at lower pressures than are often required. Hence in most mineral-water factories the ***continuous process*** is employed. Although numerous patents

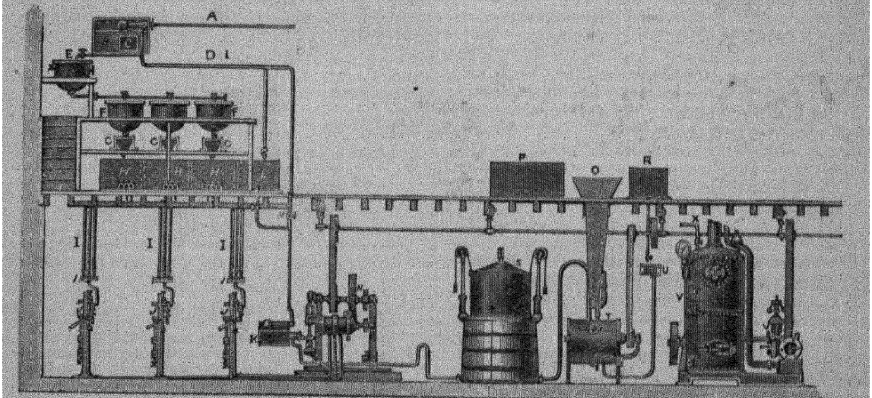
Principal Saline Constituents of Mineral Waters—Parts per 10,000.

Source	Sodium carbonate	Sodium chloride	Sodium sulphate	Potassium carbonate	Potassium chloride	Potassium sulphate	Magnesium carbonate	Magnesium sulphate	Calcium carbonate	Iron oxide and alumina	Carbon dioxide per litre	Authority
											c.c.	
Apollinaris .	12·57	4·66	3·00	trace	—	—	4·42	—	0·59	0·20	—	Bischoff and Mohr
Hunyadi Janos	7·96	13·05	159·15	—	—	0·85	—	160·16	9·33	0·04	—	Knapp
Kissingen .	0·04	74·21	2·28	—	0·32	—	2·10	—	7·74	0·24	1026 at 11°C.	Kastner, Bauer, and Struve
Selters . .	8·01	22·51	—	—	0·47	0·51	2·60	—	2·43	—	1087 at 15°C.	Struve
Vichy . .	48·83	5·34	2·91	3·52	—	—	3·30	—	4·34	trace	508	Bouquet
Wiesbaden .	—	68·35	—	—	1·46	—	—	—	4·18	—	200	Fresenius

in connection with aërating machinery have been taken out, the type of machine which originated with Bramah is still the one in general use.

In Bramah's continuous process the gas is generated in a leaden or lead-lined generator from sulphuric acid and a carbonate, and passes into a gasometer consisting of an inverted copper bell in a tank of water. Thence, after expanding, it is pumped, simultaneously with water, into a condenser or globe, where the water is finely divided and saturated with the gas under a pressure indicated upon a gauge. From this it passes into the bottling part of the machine, where each bottle, placed by hand in position, receives a measured quantity of concentrated sodium carbonate solution or of sweetened syrup and is filled up with the water charged with the gas.

A 'blow-off' valve is provided so that the



Plan of a Soda-water Manufactory.

A. Main water supply from well or waterworks.
B. Water reserve.
C. Filter.
D. Pipe and branches supplying filtered water to syrup boiler, solution tank, and soda-water machine.
E. Steam-cased pan for boiling syrups.
FFF. Mixing and cooling pans for syrups.
GGG. Felt filtering bags, through which syrup is passed.
HHH. Tank in compartments for storing filtered syrups.
III. Syrup junctions and pipes supplying syrup pumps at bottling machines.
JJJ. Bottling machines
K. Solution pan feeding soda-water machine with either plain water from filter C, or soda or other solution from tank L.
L. Soda-water solution tank for mixing mineral waters which require no syrup. When using this tank the tap M is closed.
M. Tap to shut off plain filtered water when bottling non-saccharine beverages.
N. Soda-water machine.
O. Condenser containing aërated water, to which pipes leading to bottling machines are attached.
P. Whiting bin.
Q. Whiting shoot to generator.
R. Vitriol cistern.
S. Gasometer.
T. Generator.
U. Blow-back prevention acid box.
V. Steam engine.
X. Steam pipe to syrup boiler and bottle-washing apparatus.

air may be completely expelled from the bottle, and in some types of machines there are means for returning the excess of gas to the gasometer, though this is not altogether advantageous

Arrangement of Apparatus—The general mode of arranging the aerating apparatus in the factory is shown in the accompanying figure (p 51) The generator, T, is now frequently replaced by cylinders of liquefied carbon dioxide, which are connected with the gasometer. The soda water machine, properly so called, has one or two pumps for forcing the gas and the water into the condenser, O, the latter being made of gun-metal with a lining of pure tin, and capable of withstanding a pressure three or four times in excess of any normally employed In small installations a gas-engine usually takes the place of a steam-engine

Carbon Dioxide Supply.—The general use of liquefied carbon dioxide instead of that generated from acid and calcium carbonate is the chief improvement on the original method of bottling. The new method is less expensive, more convenient, and obviates the difficulty attending the older process of disposing of the residue of calcium sulphate from the generator

Liquefied carbon dioxide collected from the fermenting tuns in breweries is sometimes employed, but in the writer's experience gas from this source not infrequently contains traces of volatile impurities, which impart an unpleasant flavour to soda-water

Pressures for Aërating—Soda-water and similar unsweetened mineral waters are usually bottled at a pressure of 100–120 lbs to the square inch in bottles, and of 150 lbs in siphons, whilst for lemonade and the like a pressure of 60–80 lbs is employed. In the case of goods intended for export a much lower pressure (usually 40–50 lbs) is generally considered sufficient The figures here given are those indicated upon the pressure gauge of the machine, the actual pressure in the closed bottle being very much less Thus experiments made by the writer have shown that the pressure within bottles of soda water bottled at a machine pressure of 100-120 lbs does not exceed 45-55 lbs An excess of pressure above a certain limit does not result in the liquid containing more gas

During the last few years automatic bottling machines have been introduced into all the leading factories

The principle upon which these machines is based is that of charging an upper cylinder with the carbonated liquid, and filling the bottles automatically in turn, after creating a counter-pressure Under these conditions the liquid flows quietly into the bottles, and there is no unavoidable loss of gas or syrup, through having to remove the air by 'snifting'

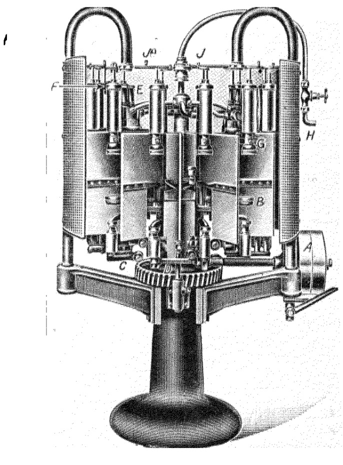
The bottles are brought beneath the filling cylinder on a rotating platform, and each in turn fits tightly into a bell mouth, while a valve is provided for the escape of the air expelled by the carbon dioxide This air collects above the liquid in the feeding cylinder, until, when a certain pressure is reached, it is automatically discharged through a valve at the top After filling, the bottles are removed by hand, and either corked by hand or by machinery, without any material loss of pressure

The larger sizes of machines are capable of filling from 100 to 140 dozen bottles per hour, and the saving in gas, as compared with the old type of filling machines, is about 25 p c

Low pressure Bottling—Machines for automatically filling the bottles at a low pressure are also largely used in mineral water factories, and have the advantage of speed over machines in which the filling is effected by the action of counter pressure

An automatic machine of this type is shown below As the machine revolves the empty bottles are successively inserted in the space above the blocks B, which are depressed in turn by the action of the lever C, and are held in position, with an air tight joint round the mouths, by means of a spring The aerated water enters the bottles from air-chambers in a spiral stream, leaving a space in the centre, through which the air escapes, and passing through a small hole in the mouth piece, is compressed in a chamber, until it is released by the removal of the bottle from the machine When the revolution is complete each bottle is removed by hand, and corked or stoppered without material loss of pressure.

By the use of either this system or the counter pressure system there is no waste of gas or liquid, and the bottles are more perfectly charged with carbon dioxide at a pressure of



HAYWARD-TYLER & CO.'S POWER THIS' FILLING MACHINE

A, Fast and loose pulleys for driving machine, B, Bottle rests on which bottles are placed for filling, C, Bottle rest levers, D, Cam, which operates bottle rest levers, E, Rollers on valve handles, F, Cam for opening valves, G, Release valves to let air out of chambers. H, Tappet for opening release valves, I, Air chambers, J, Regulating handles for air chambers

75-80 lbs than was possible on the older types of machines, in which a pressure of 120 lbs or over was commonly used, and the air was expelled from each bottle by means of a 'snifting' valve controlled by hand

An essential of good bottling is that all air should be expelled from the bottle, since otherwise, air being only slightly soluble as compared with carbon dioxide, the liquid will rush with almost explosive violence from the bottle, when opened, but will become flat almost immediately On the other hand, a liquid properly saturated with carbon dioxide and free from air will continue to emit minute bubbles of gas for at least five minutes after it leaves the bottle.

Pressure Gauges—The mode of measuring the pressure of the gas varies in different countries. Thus in England and the United States the zero mark on the dial of the pressure gauge indicates atmospheric pressure, and the succeeding figures represent the number of lbs in *excess* of that pressure In Germany the dial is graduated in atmospheric pressures in excess of the normal pressure, which is represented by zero; whereas in France, which adopts the same mode of expression, the figure 1 represents the normal pressure, and the figure 2 corresponds to 1 on the German scale and to 15 lbs on the British and American scales, and so on

Sweetened Aërated Drinks—Lemonade, ginger ale, and similar sweetened 'mineral waters' are prepared in the same way as soda water A thick syrup is made from sugar and saccharin and water, and this is acidified with citric or tartaric acid and flavoured with an essential oil, which is conveniently added in the form of an alcoholic solution termed a 'soluble essence'

The syrups are filtered through the filter bags shown at C, C, C, in the diagram, into their respective tanks, H, H, H, whence they are drawn off into the bottling machine The use of saccharin to replace part of the sugar in the syrups is almost universal in this country. It has the advantages of reducing the cost and of acting as a preservative, whilst its disadvantages are its cloying taste, which prevents its being used in more than a certain proportion, and the want of fulness on the palate of syrups containing it. The latter drawback is sometimes remedied by the addition of glucose syrup

Methods of detecting and identifying saccharin are described by Boucher and Bourgne, Bull. Soc Chim Belg 1903, 17, 126, Analyst, 1903, 28, 241, von Maler, Farmaz J 1904, 1089; Analyst, 1904, 29, 374, Villiers, Ann Chim. Anal 1904, 9, 418; Analyst, 1905, 30, 21, Chace, J Amer Chem Soc 1904, 26, 1627, Jorgenson, Analyst, 1909, 34, 156.

Addition of Saponin—The popular demand for a liquid which shall retain a frothy head for some time after it has left the bottle has led to the manufacturers frequently adding an extract of quillaia bark or other preparation of saponin, sold under the name of 'foam heading,' &c. Such an addition is more necessary in liquids containing saccharin than in all sugar beverages, which froth more with the carbon dioxide According to the results of experiments made by Lohmann (Zeitsch offentl. Chem. 1903, 9, 320, Analyst, 1903, 28, 361), saponin has no injurious physiological effects On the other hand, according to Bourcet and Chevalier (Pharm. J 1905, 75, 691) commercial saponin contains neutral saponins of a toxic nature

For the detection of saponin, *see* Brunner (Zeit Untersuch Nahr Genussm 1902, 5, 1197), and Ruhle (*ibid* 1908, 16, 165; J Chem Soc Ind 1908, 27, 954), Rosenthaler (Zeit Untersuch Nahr Genussm 1913, 25, 154), and Campos (Ann Chim. anal 1914, 19, 289).

Fermented Beverages—The products of the mineral water factory include one or two beverages in which the aeration is the result of a limited fermentation

Ginger beer, which is the type of this class, is prepared by adding sugar and citric acid to a dilute infusion of ginger root, infecting the liquid with a small quantity of a suitable yeast, bottling it, and allowing the bottles to stand at a proper temperature until sufficient fermentation has taken place

As a rule the fermented liquid contains less than 1 p c of absolute alcohol, but occasionally in very hot weather the fermentation may proceed much further, and the ginger beer may then contain as much as 5 or 6 p c of alcohol. The pressure in the bottle of ginger beer when ready for consumption averages about 15 lbs to the square inch, but in cases of abnormal fermentation it may reach 100 lbs or more, and burst the bottle

Occasionally objectionable flavours are produced by infection of the liquid with wild yeasts or bacteria, just as in the case of ordinary beer

Other drinks of this description are horehound beer and other herb beers. Certain non-alcoholic ales on the market are prepared by partial fermentation of an infusion of malt and hops, which is then used as a syrup, and bottled with aerated water as in the case of lemonade

Stoppers of Bottles—The screw stopper of vulcanite or stoneware with a rubber ring to effect a tight joint is now universally employed, for the glass ball stopper (which had much to recommend it) has fallen into popular disfavour, and is now rarely met with, except in out-of-the-way districts

The chief objection to the rubber-clad stopper is that impurities of various kinds may lodge beneath the rubber, and unless strict cleanliness is observed, may contaminate the contents of the next bottle into which it is introduced.

The Crown corking system has in recent years come into general favour for closing bottles of mineral water

A cap of tinned steel or aluminium, with a corrugated edge, is pressed down by a machine into a special ridge on the neck of the bottle, while a disc of prepared sterilised cork covered with parchment paper, which is fitted into the cap, makes an air tight joint

It is essential that the bottles should be of an exact pattern, since the slightest variation from the standard may lead to faulty bottling and consequent loss of gas

Bacteriological Conditions—It was formerly believed that sterilisation was effected by aerating a liquid with carbon dioxide under a high pressure In 1908, however, bacterioscopic examinations were made, at the instigation of the medical officer for the City of London, of a large number of bottles of soda-water, and it was found that about 25 p.c. could be regarded as pure, and over 33 p.c. as impure, the remainder being 'fairly pure' or 'not pure.' In some of the worst samples the numbers of micro-organisms per 1 c.c. at 20° were uncountable, and some yielded sediment from 50 c.c., which when cultivated at 37°, gave innumerable colonies.

As the result of this investigation a meeting of representative mineral water manufacturers was held, and it was decided to adopt stringent measures to guard against bacterial contamination.

In addition to the obvious precautions of having a pure water supply and observing cleanliness in every stage of the manufacture, it was agreed to discard all wooden tanks and vessels (except for preliminary soaking to remove labels from old bottles), to rinse the bottles with water of assured purity immediately before filling, and to use for this purpose a metal jet of sufficient force. Wherever practicable, rubber rings were to be removed from the stoppers, or, failing that, were to be immersed in a solution of calcium bisulphite, and afterwards rinsed with pure water. The plant was also to be inspected by a competent authority.

There is no doubt that the adoption of such precautions has had the result of raising the standard of purity of soda-water throughout the country.

In considering the bacteriological aspect of the question, several points suggest themselves. Thus an unfavourable bacterioscopic examination of one or two samples taken casually does not necessarily imply faulty manufacture, for it may be the result of accidental contamination of the stopper by the hands of the worker—against which there is no complete safeguard.

Absolute sterility of the contents of the bottle should not be demanded, and it is unreasonable to require a greater degree of purity than that of the average water supply of London. Given a sufficient degree of purity of the original water, which is essential, efficient inspection of the factory at irregular intervals is a better protection than an occasional bacterioscopic examination. When such examinations are made periodically, they should be made under comparable conditions, *i.e.* at the same intervals after bottling; otherwise the product of the cleaner process may show the worse results.

Standards are notoriously difficult to fix, but making allowance for the various chances of contamination, an average sample of soda water, examined one day after bottling, should not yield more than 100 organisms per 1 c.c. at 20°, or contain sufficient *B. coli* to be discoverable in 10 c.c.

Preservatives in Mineral Waters.—The preservatives most likely to be met with in unsweetened mineral waters are sulphites and bisulphites, solutions of which are frequently used, as in breweries, for cleansing the plant.

A small proportion of salicylic acid is often employed to prevent fermentation in the so-called 'fruit syrups' and other sweetened articles, which might otherwise ferment and be the subject of an excise prosecution for containing alcohol.

Fermentations occurring in Mineral Waters.—Excessive fermentation of ginger beer is not uncommon in very hot weather, and the writer has met with samples containing as much as 6 p.c. of absolute alcohol.

Occasionally acetic or lactic fermentation may take place, and spoil a batch of goods, but this seldom happens when thorough cleanliness is observed.

A troublesome form of fermentation, commonly termed the 'mucoid fermentation,' results in the conversion of the contents of the bottle into a thick ropy gelatinous mass. This may be caused by several micro-organisms, such as *B. gelatinosum betæ* or *B. viscosus sacchari*, and is more liable to occur when beet sugar is used for the syrup than when cane sugar is used. When it occurs in an isolated bottle, insufficient cleansing is a chief factor in its production.

Metallic Impurities.—Mineral waters not infrequently contain traces of metallic impurities, especially iron, tin, and lead, derived from the materials used or from some part of the plant.

Iron in soda-water is objectionable from the fact that, when the beverage is added to a light-coloured liquid, such as whiskey, containing a trace of tannin, an unpleasant dark colouration is produced.

Traces of tin find their way into mineral waters through the action of acid syrups upon the tin piping leading to the bottling machines, whilst lead may be derived from solder on the pipes. No such soldering should be permitted, and thorough flushing of tin piping with water night and morning effectually prevents contamination with tin. A still better safeguard, which has been adopted by some factories, is to replace the tin pipe by glass tubes with rubber connections.

Alloys of lead or antimony with tin are more soluble in seltzer water than either metal separately (*see* Barillé, Compt. rend. 1911, 153, 351).

A still more common source of lead is the citric or tartaric acid, in which it is frequently present as a manufacturing impurity.

Copper is not a common impurity, and, when present, is usually due to accidental contact of the acid syrup with the metal.

Arsenic may be derived from glucose used in the preparation of the syrups, or from the use of preparations of phosphoric acid instead of citric or tartaric acid for acidifying the syrups.

It has been asserted that mineral waters take up traces of antimony from the rubber rings of the stopper (which contain a large proportion of antimony sulphide). Experiments made by the writer, however, have shown that even a boiling 5 p.c. solution of hydrochloric acid does not dissolve any antimony from red rubber, and that there is thus no risk of mineral waters being contaminated in this way.

(For the detection of traces of metallic impurities in mineral waters, *see* Budden and Hardy (Detection of Lead, Tin, Copper, and Iron), Analyst, 1894, 19, 169; Tatlock and Thomson (Lead in Citric and Tartaric Acid), Analyst, 1908, 33, 173; Lander and Winter (Poisonous Metals), Analyst, 1908, 33, 450; Report of Conjoint Committee on Arsenic Determination, Analyst, 1902, 27, 48; Report of Royal Commission (Arsenic), Analyst, 1904, 29, 60; Thorpe (Electrolytic Determination of Arsenic), Analyst, 1903, 28, 349); Curtman and Mosher (tin), J. Amer. Chem Soc. 1913, 35, 357). C. A. M.

ÆRGUO. (Verdigris (?) or hydrated basic carbonate of copper.) The name given by the Romans to the green rust produced on copper and bronze by the united action of the oxygen water and carbon dioxide of the air. It was considered by them to enhance the beauty of their bronze statues. The same rust forms on brass, which was, however, not used by the Romans.

ÆSCHYNITE. A rare-earth mineral from Miask in the Ilmen Mountains, southern Urals, described by Berzelius in 1828, and named from *αἰσχύνη*, shame, in allusion to the fact that at that time no means of separating titanium and columbium was known to chemists. It is a titano-columbate (and thorate) of cerium-metals, calcium, and iron, and the composition can be expressed as a combination of a meta-columbate $(Ca,Fe)Cb_2O_6$ with a titanate (and thorate) $Ce_2(Ti,Th)_4O_{11}$. The mineral forms orthorhombic crystals of prismatic habit. It is black or brownish, with a pitchy lustre, and conchoidal fracture; sp.gr. 4·9–5·17; hardness, 5–6. The crystals are found with red felspar, biotite, and zircon in nepheline-syenite at Miask, Urals. The mineral from Hitterö, Norway, referred to this species by W. C. Brogger in 1879, has since been named blomstrandine (*q.v.*). L. J. S.

ÆSCULETIN, ÆSCULIN *v.* GLUCOSIDES and HORSE CHESTNUT.

AETHUSA CYNAPIUM (Linn.). 'Fool's parsley' or the 'lesser hemlock,' a poisonous umbelliferous herb When dried and extracted with alcohol, yields on distillation a small quantity of an essential oil, and the residue contains a resin, a crystalline hydrocarbon *pentatriacontane* $C_{35}H_{72}$ (m.p. 74°) and a crystalline alcohol (m.p. 140°–141°: $[\alpha]_D = -35{\cdot}7°$) either isomeric with phytosterol $C_{26}H_{44}O$, or a lower homologue; *d-mannitol*, together with a small quantity of a *volatile alkaloid* resembling conine, to which the alleged poisonous character of the herb may be due (Power and Tutin, J. Soc. Chem. Ind. 1905, 938).

AFFINITY, CHEMICAL *v.* CHEMICAL AFFINITY.

AFRICAN ELEMI *v.* OLEO-RESINS.

AFRICAN GREEN or **EMERALD GREEN** *v.* PIGMENTS.

AFRICAN INCENSE *v.* OLEO-RESINS.

AFRICAN MARIGOLD. *Tagetes patula.* *Quercetagetin* was isolated from the flowers of the African marigold, *Tagetes patula*, by Latour and Magnier de la Source (Bull. Soc. chim. 1877, [ii.] 28, 337), who state that it also occurs in other varieties of the same plant. In appearance and general properties it is described as resembling quercetin, the colouring matter of quercitron bark, and from this fact, together with its origin, the name *quercetagetin* is evidently derived. On the other hand, according to these authors, its crystalline form, solubility in 60 p.c. alcohol, and the numbers obtained on analysis indicated that it was distinct from quercetin $C_{27}H_{20}O_{12}$, and it was considered to possess the formula $C_{27}H_{22}O_{13}$ (anhydrous) or $C_{27}H_{22}O_{13},4H_2O$ (air-dried). A preliminary re-examination of this colouring matter was made by Perkin in 1902 (Chem. Soc. Proc. 18, 75), and it has more recently been studied in greater detail by the same author (Chem. Soc. Trans. 1913, 103, 209). To isolate the colouring matter, which is largely present in the flowers as glucoside, a concentrated alcoholic extract is diluted with water which precipitates a viscous impurity, and this is removed by means of ether. The clear liquid treated when boiling with addition of a little hydrochloric acid deposits after cooling but a small bulk of the colouring matter, and repeated extraction of the solution with ether is necessary for its economical isolation. The crude product thus obtained can be crystallised from dilute alcohol, but for complete purification it is necessary to prepare the acetyl derivative, and after re-crystallisation to hydrolyse this in the usual manner.

Quercetagetin $C_{15}H_{10}O_8$, or as crystallised from dilute alcohol $C_{15}H_{10}O_8,2H_2O$, forms pale yellow glistening needles or leaflets resembling quercetin in appearance and melts at about 318°. Very dilute alkali dissolves it with a pure yellow colour, which by air oxidation becomes olive, and finally deep brown, but these changes are not so marked when a stronger alkali (10 p.c.) is employed. Alcoholic ferric chloride produces an olive-green colouration, whereas cold alcoholic lead acetate forms an orange-red precipitate which on keeping becomes yellower and finally develops a green tint. On fusion with alkali *protocatechuic acid* is obtained, together with a phenolic product which, however, quickly oxidises, and has not yet been identified.

Quercetagetin readily yields oxonium salts with mineral acids, and of these the *sulphate* $C_{15}H_{10}O_8,H_2SO_4$, fine orange-coloured needles, has been described.

Monopotassium quercetagetin $C_{15}H_9O_8K$ separates as an orange-yellow semi-crystalline precipitate when potassium acetate is added to a solution of quercetagetin in absolute alcohol.

By acetylation *acetylquercetagetin*

$$C_{15}H_4O_8(C_2H_3O)_6$$

colourless needles, melting at 209°–211°, is produced and on alkylation employing alkyl iodide *quercetagetin pentamethyl ether* $C_{15}H_5O_3(OCH_3)_5$, pale yellow needles, m.p. 161°–162°, and *quercetagetin hexamethyl ether* $C_{15}H_4O_2(OCH_3)_6$, colourless needles, m.p. 157°–158°, can be prepared. *Acetylquercetagetin pentamethyl ether*

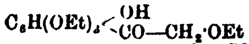
$$C_{15}H_4O_3(OCH_3)_5C_2H_3O,$$

melts 161°–163°.

Quercetagetin hexaethyl ether $C_{15}H_4O_2(OEt)_6$ m.p. 139°–141°, yields oxonium salts with mineral acids in the presence of acetic acid, the sulphate separating in orange needles, whereas the crystals of the hydrochloride possesses a somewhat more yellow colour. This behaviour is analogous to that of quercetin pentamethyl ether (Watson, Chem. Soc. Proc. 1911, 27, 163).

When hydrolysed with alcoholic potassium hydroxide quercetagetin hexaethyl ether gives *protocatechuic acid diethyl ether* and *quercetagetol tetraethyl ether* $C_{18}H_{24}O_6$, which crystallises in prismatic needles, m.p. 46°–48°. The latter yields the oxime $C_{18}H_{25}O_6N$, m.p. 93°–95°, and when oxidised with alkaline permanganate *quercetagetinic acid*, m.p. 100°–102°, is produced.

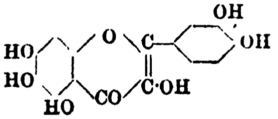
The production of quercetagetol diethyl ether to which the constitution (1) is assigned, and protocatechuic acid diethyl ether (2)

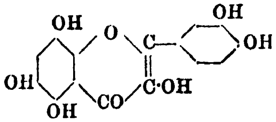
(1) 

$$C_6H(OEt)_4<\begin{matrix}OH\\CO—CH_2·OEt\end{matrix}$$

(2) $CO_2H·C_6H_3(OEt)_2$

from quercetagetin hexaethyl ether, indicate that quercetagetin is a pentahydroxyflavonol isomeric with myricetin and gossypetin. Similarly to this latter colouring matter it appears to contain a tetrahydroxybenzene nucleus, and it is suggested that its constitution may be represented by one of the two following formulæ:





Quercetagetin readily dyes mordanted fabrics shades of a generally similar character to those given by other well-known flavonol colouring matters.

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Dull olive-yellow.	Yellow-orange.	Brown.	Brownish-black.

A trace of a more sparingly soluble colouring matter is present in the flowers and represents about 1 p.c. of the crude quercetagetin referred to above. It crystallises from alcohol in somewhat indefinite groups of minute needles and dissolves in alkaline solutions with an orange colour passing to green on dilution with water. Though similar in appearance to rhamnetin (quercetin monomethyl ether) it does not contain a methoxy group.

Dyeing Properties of the Flowers.—Employing mordanted woollen cloth, the following shades are produced:—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Yellowish-brown.	Pale dull yellow.	Deep yellow-orange.	Brownish-black.

These possess a somewhat redder character than those given by quercitron bark, and are similar to, though not so red as those from patent bark. As quercetagetin mainly occurs in the flowers as glucoside, their tinctorial effect is evidently due to this latter. A. G. P.

AFRIDOL. Trade name for the sodium salt of hydroxymercury-*o*-toluic acid.

AGALITE. A name used in the paper-making trade for a fibrous variety of the mineral talc, a hydrated magnesium silicate, $H_2Mg_3Si_4O_{12}$. It is white with a tinge of green, and is readily reduced to short, fine fibres. It is obtained almost exclusively from the district near Gouverneur, in St. Lawrence Co., New York, about 70,000 tons, valued at $10 per ton, being produced annually, practically all of it being used in the American paper trade. It gives weight and body, and produces a fine gloss on the surface of the paper. L. J. S.

AGALMATOLITE, or Pagodite. A soft stone much used in the East, especially in China, for carving small statues and figures, as signified by these names. At least three mineral species appear to be included under these terms, viz. pyrophyllite, steatite, and pinite; but it is to the compact forms of the first of these that they are perhaps more generally applied. In addition to their compact nature and low degree of hardness, they have in common a greasy or soapy feel: in colour they are white, greyish, greenish, yellowish, &c., often with mottling. Pyrophyllite is a hydrated aluminium silicate, $H_2Al_2Si_4O_{12}$; steatite, a hydrated magnesium silicate, $H_2Mg_3Si_4O_{12}$; and pinite is an alteration-product consisting largely of a finely scaly muscovite-mica, a hydrated potassium aluminium silicate, $H_2KAl_3Si_3O_{12}$. Besides being employed as material for carving, these minerals are used for slate-pencils ('pencil-stone') and for tailor's chalk ('French chalk').

Extensive beds of compact pyrophyllite are quarried in the Deep River region in North Carolina, the material being mainly used for making slate-pencils. At Fukuye, in Goto Island, in the south of Japan, a compact mineral allied to pyrophyllite is mined under the name of 'rōseki' (meaning 'greasy stone' in Japanese); it is crushed, washed, and prepared very much like china-clay, and the product used for making fire-bricks, and to a smaller extent in the manufacture of porcelain and paper. This material contains SiO_2 53–58, Al_2O_3 32–36, H_2O 7–9 p.c. L. J. S.

AGAR-AGAR. Bengal Isinglass. Dried seaweed obtained from Singapore and other places. It is obtained from various red algæ, including *Gelidium corneum*, *G. cartilagineum*, *Eucheuma spinosum*, and *Gracilaria lichenoides*, which grow along the coasts of Eastern Asia and Malaya. The cell-walls of these seaweeds, when placed in boiling water, change into jelly.

It occurs in small transparent strips or as a powder, and dissolves almost entirely in water to a gelatinous, tasteless, and inodorous jelly. It is widely used as a nutritive medium for the cultivation of bacteria and fungi. Analysis of fifteen samples of agar from widely different sources gave the following results: moisture, 14·57–17·84 (average 16·57); protein ($N\times6·25$), 1·53–3·26 (2·34); nitrogen-free extract, 72·72–78·21 (76·15); ether extract, 0·17–0·45 (0·30); crude fibre, 0·39–1·50 (0·80); ash, 3·08–5·68 (3·85); and silica, 0·31–1·11 (average 0·68) p.c. A specially purified commercial agar for bacteriological purposes contained: moisture, 5·72; protein, 1·14; nitrogen-free extract, 89·25; ether extract, 0·32; crude fibre, 0·45; ash, 3·12; silica, 0·29 p.c. High ash or silica content is indicative of an inferior product. An aqueous solution of agar is acid to phenolphthalein. A purified agar for use in bacteriological work where a gelatinising agent containing a minimum of nutrients is desired, may be prepared by washing agar shreds in a dilute solution of acetic acid, washing out the acid, dissolving the agar to a 5 p.c. solution, and pouring the hot solution slowly into a large volume of 95 p.c. alcohol or acetone. The precipitated agar contains considerably less nitrogen than the original material. Part at least of the nitrogen compounds present in agar is available as nutriment for micro-organisms. The setting power of aqueous solutions of agar is not destroyed by acid or alkali between the limiting concentrations of 4·5 p.c. HCl and 5 p.c. NaOH; but if the solution be heated for fifteen minutes under a pressure of 1 atmosphere, the range of concentrations within which solidification occurs is reduced to from 2 p.c. HCl to 4·5 p.c. NaOH. The gelatinising power is increased by addition of peptone and slightly diminished by potassium chloride (Fellers, J. Ind. Eng. Chem. 1916, 8, 1128; J. Soc. Chem. Ind. 1917, 36, 43). *See* also ALGÆ and GUMS.

AGAROBILLA. The seed-pods of *Cæsalpina brevifolia* (Baill.), used in dyeing and tanning.

AGATE. A native form of silica consisting mainly of chalcedony (*q.v.*) and showing a more or less concentric arrangement of differently coloured layers or bands. The layers differ not only in colour, but also in translucency, porosity, and crystalline structure. Some layers show the minutely fibrous structure of typical chalcedony, others are more dense and cryptocrystalline, while some may consist of crystalline quartz, or again of opaline silica. Some of the layers containing larger amounts of impurities and colouring matter may be more of the character of jasper, as in the agate-jaspers or jasp-agates. The material has been deposited layer upon layer from solution in a colloidal form, and subsequently solidified in a partly crystallised condition. The deposition has taken place as a lining in rock cavities, proceeding inwards from the margins of the cavity. In the majority of cases the containing rock is a volcanic rock of basic composition (*i.e.* containing no free primary quartz); the commonest home of the agate being the steam cavities of basaltic rocks. The movement of the molten lava has caused the steam cavities, originally spherical, to be drawn out into almond shapes in the direction of the flow. These almond-shaped, or amygdaloidal, cavities may subsequently become filled with secondary mineral matter of various kinds, derived from the primary minerals of the rock by the action of the hot vapours and solutions which are always present in igneous magmas. Such secondary minerals—calcite and various zeolites—which are commonly associated with agates, have probably been formed while the rock was still hot. The exact conditions of deposition and mode of formation of agates have, however, given rise to much discussion. With the weathering of such an amygdaloidal rock the agate-amygdales, being more resistant, are set free, and may be easily separated from the clayey matrix, or they are washed away and broken up in streams and rivers.

The artificial deposition of gelatinous silica in forms closely resembling those of certain agates has been effected by J. I'Anson and E. A. Pankhurst (Mineralogical Magazine, 1882, v. p. 34). A strong acid is introduced by means of a pipette into a solution of an alkaline silicate containing a certain proportion of alkaline carbonate; the bubbles of carbon dioxide set free become coated as they ascend with gelatinous silica. Agate like structures have also been produced by Liesegang by the diffusion of one saline solution into another in a gelatinous medium (R. E. Liesegang, Geologische Diffusionen, Dresden and Leipzig, 1913; Die Achate, Dresden and Leipzig, 1916).

Many trivial varieties of agate are distinguished, depending on the patterns presented by the several layers of the stone. For example, fortification-agate, eye-agate, ring-agate, riband-agate, brecciated-agate, &c. *Onyx* is an important variety, differing simply in that the layers are plane, thus enabling cameos to be engraved in relief in one layer with a background in another differently coloured layer. A typical onyx with alternately white and black layers is however, of rare occurrence in nature, and has usually been produced by artificial colouring, as explained below. In carnelian-onyx the layers are red and white, and in sardonyx brown and white. Moss-agates, mocha-stones, dendrites, &c., are chalcedonies with enclosures of various kinds.

The artificial colouring of banded chalcedony, or the intensification of the coloration of agates, for the production of ornamental objects was probably known to the ancient Romans, and was practised by the Italian cameo-workers of the Middle Ages. The art was for a time lost, and again came into use at Idar in Germany about the year 1820, where it has been much developed and extensively used. Indeed, practically all the fashioned and polished stones now placed on the market have been artificially treated.

A *black* colour is obtained by soaking the well-dried stones for some weeks in a warm dilute solution of sugar or honey, or in olive-oil, and, after washing, immersing them in warm sulphuric acid. The organic matter absorbed by the more porous layers of the stone is thus carbonised. In case the black colouration is too intense it may be softened by the action of nitric acid. A rich *brown* colour has recently been produced in some translucent stones, giving them somewhat the appearance of garnet, by soaking them in brown sugar-candy and then igniting. A *red* colour is produced by saturating the stone with a solution of an iron salt and igniting. A *yellow* tint inclining to lemon-yellow, is imparted by digesting the stones in warm hydrochloric acid. *Blue*, ranging from the deepest indigo to delicate sky-blue, is produced by soaking the stones first in a solution of ferrous sulphate and afterwards in a solution of potassium ferrocyanide. Such a colour, and also lemon-yellow, is, however, unknown amongst naturally coloured agates. The blue coloured stones have often been passed off as lapis-lazuli, but they are readily distinguished from this by their greater degree of translucency and hardness, and the absence of specks of iron-pyrites. *Green* colours, resembling that of the natural chrysoprase, have been produced by the use of salts of chromium and nickel. Finally, various fancy and quite unnatural colours have been produced by simply dyeing the stones with aniline dyes; these colours fade on exposure to light, and finally disappear. On the history of colouring agates, *see* Nöggerath, Die Kunst, Onyxe . . . zu färben, Karsten's Archiv, 1848, xxii. 262; and on the methods now in use at

Idar, O. Dreher, Das Färben des Achats, Idar, 1913.

The agate-cutting industry has long been centred at Idar and Oberstein on the Nahe, a tributary of the Rhine, and originally the stones were obtained locally from the amygdaloidal melaphyre of the Galgenberg. But since 1827 enormous quantities have been imported from Uruguay and the neighbouring Brazilian state of Rio Grande do Sul. In India, agates and other varieties of chalcedony are abundant in the trap rocks of the Deccan plateau, and have long been worked by the native lapidaries. The well-known 'Scotch pebbles' are prettily coloured agates from Forfarshire, Perthshire, &c. Many localities in America and Australia might also be cited.

Besides being used for a great variety of small ornamental objects, agate finds technical applications in the construction of pestles and mortars, burnishers for gold-workers and bookbinders, smooth stones for paper and card manufacturers, rollers for ribbon makers, and pivot supports for balances, magnetic needles, &c. It may be remarked, however, that an 'agate mortar' need not necessarily show the coloured banding of a true agate, but may just as well be cut from an unbanded chalcedony.

On the agate industry, *see* G. Lange, Die Halbedelsteine . . . und die Geschichte der Achatindustrie (Kreuznach, 1868); Upmann, Beit. z. Gesch. d. Graftsch. Oberstein (Mainz, 1872). On Scotch agates, *see* Guide to the Collection of Scottish Agates, Royal Scottish Museum (Edinburgh, 1899); M. F. Heddle, The Mineralogy of Scotland (Edinburgh, 1901). On agate in general, *see* M. Bauer, Edelsteinkunde, 2nd edit. (Leipzig, 1909), and Engl. transl., Precious Stones, by L. J. Spencer (London, 1904); R. Brauns, transl. by L. J. Spencer, The Mineral Kingdom (Esslingen, 1912).

L. J. S.

AGAVE. An amaryllidaceous genus including several species, the leaves of which provide useful fibres. 'Pite,' or 'pita hemp,' mainly produced in Mexico, is obtained from *A. americana* (Linn.) and *A. mexicana* (Lam.). It is also obtained from several other American species of *Agave*. 'Sisal hemp' is derived from *A. rigida* (Mill.), which grows in Mexico, Central America, and the West Indies.

AGAVOSE. An inactive sugar $C_{12}H_{22}O_{11}$, reducing alkaline copper tartrate, and yielding a lævogyrate sugar on inversion; found in *Agave americana* (Linn.), grown in Mexico. The young flower heads are used in the preparation of a fermented intoxicating drink termed 'pulque' (Michaud and Tristan, J. Amer. Chem. Soc. 14, 548). According to Stone and Lotz, J. Amer. Chem. Soc. 17, 368, this sugar is saccharose.

AGMATINE *v.* Ergot.

AGNIN or **AGNOLIN.** Syn. for *Adeps lanæ*, or purified wool fat.

AGOBILIN. Trade name for a mixture of strontium cholate and salicylate with diacetylphenolphthalein.

AGONIADA BARK. The bark of *Plumiera lancifolia* (Muell.), used in Brazil as a remedy for intermittent fever, contains a bitter crystalline glucoside, *agoniadin* (Peckolt, Arch. Pharm. [2] 142, 40, 1870), identical with the *plumieride* of Boorsma and Merck, obtained from *Plumiera acutifolia* (Poir.); it is probably the *methyl ester of plumieridic acid*, and has the composition $C_{21}H_{26}O_{12}$ (*cf.* Franchimont, Rec. trav. chim. 1898, 18, 334; Proc. K. Akad. Wetensch. Amsterdam, 1900, 3, 35).

AGROPYRUM (B.P.) or **TRITICUM.** The dried rhizome of *Agropyron repens* (Beauv.).

AGROSTEMMA SAPOTOXIN *v.* Glucosides.

AGURIN. Trade name for an addition product of sodium theobromine and sodium acetate.

AGUTTAN. Oxyquinoline salicylic acid.

AICH METAL. An alloy patented by J. Aich in 1860 for use as sheathing for ships. Contains copper, 60 parts; zinc, 38·5 parts; iron, 1·5 parts.

AILANTHUS BARK. The inner bark of *A. excelsa* (Roxb.) and *A. glandulosa* (Desf.); it has the odour and taste of cinnamon; used as a tonic in dyspepsia (Dymock, Pharm. J. [3] 7, 309). An Indian name of the former is *Maharukh*.

AIROFORM. Identical with airol (*q.v.*).

AIROGEN. Identical with airol (*q.v.*).

AIROL. A basic bismuth-oxyiodide gallate, analogous to 'dermatol,' a basic bismuth-gallate. Is a greyish-green powder without smell or taste, soluble in caustic soda or dilute mineral acids. Becomes red on exposure to damp air. Has been used clinically as a substitute for iodoform (*v.* Bismuth and Iodoform).

AJOWAN OIL *v.* Oils, Essential.

AKAZGINE *v.* Nux Vomica.

AK MUDAR, AKANDA, AKRA RUI, or **ERUKKU ERUKKAM.** The bark of *Calotropis gigantea* (Ait.) and *C. procera* (Ait.). An important Indian drug (Dymock, Pharm. J. [3] 10, 122).

AKOLA *v.* Ankool.

AKRA RUI *v.* Ak Mudar.

ALABANDITE. *Manganese sulphide* (MnS) (*v.* Manganese).

ALABASTER. (*Albâtre*, Fr.; *Alabaster*, Ger.) A massive, crystalline, and marble-like variety of the mineral gypsum ($CaSO_4,2H_2O$). It is found in Glamorganshire; at Syston in Leicestershire; at Tutbury, near Burton-on-Trent in Staffordshire, and other places in Britain. A snow-white alabaster much used for small ornamental objects, such as vases, lamps, stands of timepieces, &c., is found at Volterra, in Tuscany. The harder varieties are worked with the same tools as marble, smoothed with pumice stone, polished with a mixture of chalk, soap, and milk, and finished by friction with a flannel.

The softer kinds may be turned or fashioned with rasping tools, fine chisels, or small files, smoothed with dried shave grass, then rubbed with a paste of putty powder or finely divided slaked lime, and polished by washing with soap, water, and lime, and finally with powdered elutriated French chalk or talc.

Alabaster may be stained by heating it to about 90° or 100°, and then dipping it into the colouring solution, which may be either metallic solutions, spirituous tinctures of natural dyes, or coloured oils (Habild, Wagner's Jahr. 28, 669).

A variety of alabaster known as onyx of Tecali, from Mexico, takes a fine polish; its colour varies from milk-white to pale-yellow and pale-green (J. 29, 1264).

ALACREATINE *v.* CREATINE.

ALAITE. Hydrated vanadic oxide $V_2O_5 \cdot H_2O$ found as blood-red, mossy growths with silky lustre at Tyuya-Muyun in the neighbourhood of the Alai Mountains in Fergana, Russian Central Asia. The uranium and vanadium deposits mined at this locality consist of vanadates of uranium, calcium, and copper, occurring as impregnations in a coarse-grained Devonian limestone (K. A. Nenadkevič, 1909).

L. J. S.

ALAMOSITE. A lead silicate $PbSiO_3$, found near Alamos, Sonora, Mexico; analogous to wollastonite $CaSiO_3$ in form, habit, and composition It occurs in radiated aggregates of minute colourless transparent fibres, which give a snow-white appearance to the mass (Palache and Merwin, Amer. J. Sci. 1909, 27, 399; J. Soc. Chem. Ind. 1909, 606).

ALANGIUM LAMARCKII *v.* ANKOOL.

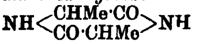
ALANINE, α-Alanine *α-aminopropionic acid* $NH_2 \cdot CHMe \cdot CO_2H$, contains an asymmetric carbon atom, and the dextro, lævo-, and racemic isomerides are known. *d*-Alanine is one of the decomposition products of a large number of proteids; together with a glucoproteid $C_7H_{14}O_4N_2$, it forms 51 p.c. of the product obtained by the hydrolysis of legumin of peas (Bleunard, Ann. Chim. Phys. [5] 26, 47), and is formed to the extent of 21 p.c. from silk fibroin (Weyl, Ber. 21, 1529; Fischer and Skita, Zeitsch. physiol. Chem. 33, 177; Johnson, J. Amer. Chem. Soc. 1916, 38, 1392–1398). It is found in yeast proteid (Neuberg, Woch. Brauerei. 1915, 32, 317–320), and in 'Zurdon's' meat extract (Zeitsch. physiol. Chem. 1913, 83, 458–467). (For the methods of separating alanine from the other hydrolytic products of the proteid, *v.* art. PROTEINS.) *r*-Alanine is prepared synthetically by the action of hydrochloric acid on the aminonitrile $NH_2 \cdot CHMe \cdot CN$, produced by the interaction of aldehyde ammonia and hydrogen cyanide (Strecker, Annalen, 75, 29); or, together with α-aminopropionitrile hydrochloride, when ammonium chloride, potassium cyanide, and acetaldehyde interact in equimolecular quantities in aqueous solution (Zelinsky and Stadnikoff, Ber. 41, 2061); by reducing α-nitrosopropionic acid with tin and hydrochloric acid (Gutknecht, Ber. 13, 1116); or hydrolysis of α-triazopropionic acid (Curtius, J. pr. Chem. [2] 38, 396).

Alanine crystallises in needles or sharp rhombic prisms, dissolves in 4·6 parts of water at 17°, or in 500 parts of 80 p.c. cold alcohol. For solubility and optical activity of *r-alanine*, *see* Pellini and Coppola (Atti R. Accad. Lincei, 1914 [v.] 23, 1, 144–150, from Chem. Zentr. 1914, 1, 124). Its heat of combustion is 389 Cal. and heat of formation 135·2 Cal. (Berthelot and André, Compt. rend. 110, 884). For quantitative estimation of the light absorbed by complex salts of alanine, *see* Ley and Hegge (Ber. 1915, 48, 70), and for the influence of neutral salts on the rotatory power of alanine, *see* Pfeiffer (Ber. 1915, 48, 1938). The resolution of racemic alanine has been effected through the benzoyl derivative, which is separated into *d-benzoylalanine* (m.p. 147°–148° $[\alpha]_D + 37 \cdot 13°$ in alkaline solution), and *l-benzoylalanine* (m.p. 150°–151° (corr.), $[\alpha]_D - 37 \cdot 3°$ in alkaline solution), by crystallisation of the brucine salt, and these yield on hydrolysis the corresponding optically active alanines; *r-alanine* decomposes at 264°–268° (Zelinsky and Stadnikoff, *l.c.*), at 293° (Fischer, Ber. 32, 2451); *d-alanine* has $[\alpha]_D + 9 \cdot 55°$ in hydrochloric acid solution; *d-alanine* is unchanged when heated with strong hydrochloric acid (Abderhalden, Zeitsch. physiol. Chem. 1912, 82, 167–172). Its aqueous solution is decomposed in presence of sunlight (Ganassini, Giorn. Farm. Chim. 61, 439–444); *l-alanine* decomposes at 297° and has $[\alpha]_D - 9 \cdot 68°$ in hydrochloric acid solution. *r-Alanine* is attacked by fermenting yeast (Ehrlich, Biochem. Zeit. 63, 379). A cultivation of *Aspergillus niger* in an aqueous solution of *r*-alanine destroys about 10 p.c. of the dextrorotatory constituent, but *Pencillium glaucum* does not flourish in a 2 p.c. alanine solution. Resolution has been effected also by means of *d*-bromocamphorsulphonic acid (Colombano and Sanna, Att. R. Accad. Lincei, 1913, [v.] 22, 11, 292–298; Gazz. chim. ital. 1914, 44, 1, 97–104).

In its physiological action, *d*-alanine causes a rapid rise in the urinary nitrogen, most of the extra nitrogen being excreted on the same day; *l*-alanine is not decomposed quite so rapidly, but none of it is excreted unchanged (Abderhalden and Schittenhelm, Zeitsch. physiol. Chem. 1907, 51, 323; compare, however, Sevene and Meyer (Amer. J. Physiol. 1909, 25, 214); when given with lactic acid it causes an increase in dextrose elimination almost equal in amount to the theoretical yield (Dakin and Dudley, J. Biol. Chem. 1914, 17, 451). After administering 20 grams of *r*-alanine, 4·7 grams of the β-naphthalenesulphonic derivative of *l*-alanine was recovered from the urine (Schittenhelm and Katzenstein, Chem. Zentr. 1906, i. 1279). When *d*-alanine is injected in the blood-stream it is rapidly absorbed, as very little can be detected in the blood or urine after a lapse of twenty minutes (Abderhalden and others, Zeitsch. physiol. Chem. 1907, 53, 113, 251, 326; 52, 507; 53, 148; 1913, 86, 478; and J. Biol. Chem. 1915, 20, 539–554).

The importance of alanine as a final hydrolytic product of many proteid substances, has led to an extensive examination of its derivatives in order to facilitate its detection (Abderhalden and Schmidt, Zeitsch. physiol. Chem. 1913, 85, 143–147; Dakin and Dudley, J. Biol. Chem. 1913, 15, 127; Chelle, Ann. Chim. anal. 1914, 19, 67) and estimation, and to determine the part it plays in the building up of the proteid molecule. A short account of the more important of these derivatives is appended.

The *copper salt* $(C_3H_6O_2N)_2Cu,H_2O$ forms bluish-violet crystals readily soluble in water. The *nickel salt* $(C_3H_6O_2N)_2Ni,4H_2O$ forms blue crystals, these become anhydrous at 108°–110° and dissolve in 132 parts of water (Orloff, Chem. Zentr. 1897, ii. 192; Bruni and Formara, Atti R. Accad. Lincei, 1904 [v.] 13, ii. 26). Complex salts are formed with heavy metals, *e.g.* $Cr(C_3H_6O_2N)_3Cr(C_3H_6O_2N)_2OH \cdot H_2O$ (Tschugaeff and Serbin, Compt. rend. 1910, 151, 1361; Ley and Winkler, Ber. 1912, 45, 372; Ley and Ficken, Ber. 1912, 45, 377; and *ibid.* 1917, 50, 1123), and with chloride of tin, *e.g.* $SnCl_4 \cdot NH_2 \cdot CHMe \cdot COOH_4$ (Fichter, Färber-Zeit. 1915, 26, 274; Chem. Zeit. 38, 693). Compounds are formed with neutral metallic salts: $LiCl\cdot(NH_2\cdot CHMe\cdot COOH)\cdot H_2O$; $CaCl^2(NH_2\cdot CHMe\cdot COOH)3H_2O$ (Pfeiffer and Modelski, Zeitsch. physiol. Chem. 1912, 85, 1–34; Pfeiffer, Ber. 1915, 48, 1938–1943). The *ethyl ester* has b.p. 48°/11 mm. and sp.gr. 0·9846 at 12·5°; *r-alaninamide*, m.p. 62° (Franchimont and Friedman, Proc. R. Akad. Wetensch. Amsterdam, 1905, 8, 475); *d-alaninamide* has m.p. 72° (corr.) and $[\alpha]_D$ +6° in 5·2 p.c. aqueous solution; *r-alanylchloride hydrochloride* $NH_3Cl\cdot CHMe\cdot COCl$ melts and decomposes at 110°; *d-alanylchloride hydrochloride* has $[\alpha]_D^{20°} +7·32°$ (Fischer, Ber. 1905, 38, 605, 2914); *r-alanineanhydride* (*dimethyldiketopiperazine*

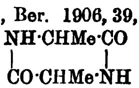


$NH{<}\substack{CHMe\cdot CO\\CO\cdot CHMe}{>}NH$ has m.p. 282°, and *d-alanineanhydride* has m.p. 297° (corr.) and $[\alpha]_D^{20°} -28·8°$ (Fischer, Ber. 1905, 39, 453). *d*-N-*Methylalanine* $CH_3\cdot CH(NH\cdot CH_3)COOH$, m.p. 165°–166° has $[\alpha]_D^{20°} +5·59°$; *l*-N-*methylalanine* $[\alpha]_D^{20°} -5·92°$; N-*benzylalanine*, m.p. about 270° (Fischer and Lipschitz, Ber. 1915, 48, 364; *ibid.* 1916, 49, 1357). *Acetylalanine* $NHAc\cdot CHMe\cdot CO_2H$ crystallises in rhombic plates $a:b:c=0·7792:1:1·0983$; m.p. 137° (de Jong, Rec. trav. chim. 19, 259; Fischer and Otto, Ber. 36, 2106); *chloracetylalanine ester* $CH_2Cl\cdot CO\cdot NH\cdot CHMe\cdot CO_2Et$ has m.p. 48·5°–49·5° (corr.) (Fischer and Otto, *l.c.*); the *benzenesulphonic derivative* $SO_2\cdot Ph\cdot NH\cdot CHMe\cdot CO_2H$ has m.p. 126° (Hedin, Ber. 1890, 23, 3197); *benzylsulphonalanine* $C_6H_5CH_2SO_2NH\cdot CH(CH_3)COOH$ has m.p. 164°–165° (Johnson, J. Amer. Chem. Soc. 1916, 38, 2135); the *β-naphthalenesulphonic derivative* $C_{13}H_{14}O_3NS$ melts and decomposes at 220° (Koenigs and Mylo, Ber. 1908, 41, 4427); the *d-camphorsulphonate* of *alanine* $C_3H_7O_2N,C_{10}H_{15}O\cdot SO_3H,H_2O$ has m.p. 105°–110° $[\alpha]_D^{18°} +14·33°$ (Colombano and Sanna, Atti R. Accad. Lincei, 1913, [v.] 22, ii. 234–237); ethyl *d-alanine-d-bromocamphorsulphonate* $CO_2Et\cdot CHMe\cdot NH_2,C_{10}H_{14}OBr\cdot SO_3H,IH_2O$ becomes anhydrous at 105°, and melts at 192°, $[\alpha]_D^{26°} +67·54°$ (Gazz. chim. ital. 44, 1, 97–104); for *hippurylalanine* $NHBz\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, m.p. 202°, and derivatives, *see* Curtius and Lambotte, J. pr. Chem. 1904, [2] 70, 109; *phthalylalanine* $C_6H_4:(CO)_2:N\cdot CHMe\cdot CO_2H$, m.p. 164°, and *phthaloylalanine* $CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CHMe\cdot CO_2H,H_2O$, m.p. 129° (Andreasch, Monatsh. 1904, 25, 774); *palmityl-a-alanine* $CH_3(CH_2)_{14}\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, m.p. 110°, $[\alpha]_D^{10°} -5·98°$ (Aberhalden and Funk, Zeitsch. physiol. Chem. 1910, 65, 61); *diethyldialaninquinone* $C_6H_2O_2(NH\cdot CHMe\cdot CO_2Et)_2$ forms red prisms, m.p. 140° (corr.) (Fischer and Schrader, Ber. 1910, 43, 525); 2:4-*dinitrophenyl-dl-alanine*, m.p. 178° (Abderhalden and Blumberg, Zeitsch. physiol. Chem. 1910, 65, 318); *d-alanine picrolonate* (Abderhalden and Weil, Zeitsch. physiol. Chem. 1912, 78, 150–155); 2-*d-alanine*-1-*picrolonic acid* has m.p. about 145° (decomposed); 1-*d-alanine*-1-*picrolonic acid*, m.p. 215°, decomposed at 217° $[\alpha]_D^{20°} +11·08°$ (Levene and Slyke, J. Biol. Chem. 1912, 12, 127–139); *d-alaninepicrolonate*, m.p. 214° (decomposes) $[\alpha]_D^{20°} +12·4°$; *dl-alanine-picrolonate*, m.p. 16° (decomposes); *benzylhydrogen-dl-alaninedithiocarboxylate* $CO_2H\cdot CHMe\cdot NHCS_2\cdot CH_2Ph$, m.p. 136° (Siegfried and Weidenhaupt, Zeitsch. physiol. Chem. 1910, 70, 152). For *dimethyl-a-alanineoxalylglycine*

$$CO_2MeCHMeNH\cdot CO\cdot CO\cdot NH\cdot CH_2\cdot CO_2Me$$

m.p. 98·5°, and other derivatives, *see* Meyeringh (Rec. trav. chim. 1913, 32, 140–157).

Among the polypeptides prepared by Fischer, Abderhalden, and others, there are many containing the 'alanyl' group one or more times, *e.g.* *r-alanylalanine* $NH_2\cdot CHMe\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, m.p. 276° (corr.), the *benzoyl derivative* m.p. 203°–204°, the *ethyl ester* m.p. 114°–116°; *dialanylalanine* $NH[CHMe\cdot CO\cdot NH]_2CHMe\cdot CO_2H$, m.p. 219° (corr.) (Fischer and Kautzsch, Ber. 1905, 38, 2375); *l-alanyl-d-alanine*, m.p. 269°–270° (corr.), $[\alpha]_D^{20°} -68·5°$; *d-alanyl-l-alanine*, m.p. 275°–276° (corr.), $[\alpha]_D^{20°} +68·94°$; (Fischer and Raske, Ber. 1906, 39, 2893, 3981), *cycloalanylalanine*



$\begin{array}{l}NH\cdot CHMe\cdot CO\\ |\qquad\qquad\quad |\\ CO\cdot CHMe\cdot NH\end{array}$ m.p. 282°–282·5° (corr.) (Maillard, Ann. Chim. Phys. 1915, [9] 3, 73); *alanyl glucosamine anhydride* $C_9H_{16}O_5N_2$ turns brown at 245°–250°, and melts at 269°–272° (Weizmann and Hopwood, Proc. Roy. Soc. 1913, A 88, 455–461); *ethylalanyl methylenemalonate* $CO_2Et\cdot CHMe\cdot NH\cdot CH:C(CO_2Et)_2$, m.p. 206°–207°; *alanyl-p-hydroxyphenylethylamine* $C_{11}H_{16}N_2O_2$, m.p. 116° (Guggenheim, Biochem. Zeitsch. 1913, 51, 369); *d-alanyl-d-aminobutyrylglycine* $CH_3CH(NH_2)CO\cdot NH\cdot CH(CO\cdot NH\cdot CH_2COOH)CH_2CH_3$, m.p. 214° (corr.) $[\alpha]_D^{20°} +13·86$ (Abderhalden, Zeitsch. physiol Chem. 1912, 77, 371–478); *d-alanylglycylleucine*

$$(CH_3)_2\cdot CH\cdot CH_2\cdot CH(NH\cdot CO\cdot CH_2NH_2)COOH$$

m.p. 132°–133° $[\alpha]_D^{20°} -13·82°$ (Abderhalden and Fodor, *ibid.* 1912, 81, 21); and the tetrapeptide *glycyltyrosyl-glycyl-d-alanine* decomposing at 225° (corr.) is probably a mixture of stereoisomerides of the tetrapeptide isolated from silk fibroin (Fischer, Ber. 1908, 41, 2860; *cf.* Abderhalden and Hirszowski, Ber. 1908, 41, 2840). For other polypeptides derived from alanine, *see* Fischer (Ber. 37, 2486; 4585; 38, 2375; 2914; Annalen, 340, 128, 152; Ber. 39, 453; 40, 943, 1754, 3717; Annalen, 363, 136), and Abderhalden (Ber. 41, 2840, 2857; 42, 3394; Zeitsch. physiol. Chem. 63, 401; 65, 417; 77, 471; 81, 21; Biochem. Zeitsch. 1913, 51, 369).

β-Alanine, *β-aminopropionic acid* $H_2N\cdot CH_2\cdot CH_2\cdot CO_2H$, prepared by treating β-iodopropionic acid with ammonia (Mulder, Ber. 9, 1902; Abderhalden and Fodor, Zeitsch. physiol. Chem. 1913, 85, 114), or with silver nitrite and reducing the resulting *nitro-* compound with tin and hydrochloric acid (Lewkowitsch, J. pr. Chem. [2] 20, 159); by heating ethyl acrylate with alcoholic ammonia in sealed tubes at 110° (Wender, Gazz. chim. ital. 19, 437); or by the action of potassium hypobromite on an alkaline solution of succinimide—this is the best method, and gives a yield of 60 p.c. of the theoretical (Hoogewerf and van Dorp, Rec. trav. chim. 10, 4; Holm, Arch. Pharm. 242, 590). It can be recognised by conversion into ethyl acrylate (Abderhalden and Fodor, Zeitsch. physiol. Chem. 1913, 85, 117).

β-Alanine forms prisms m.p. 196° (Hoogewerf and van Dorp, *l.c.*), does not melt at 220° (Kursda, Monatsh. 12, 242), m.p. 206°–207° (Lengfeld and Stieglitz, Amer. Chem. J. 15, 504); needles, m.p. 200° (Abderhalden and Fodor, *l.c.*); the hydrochloride of the *methyl ester* has m.p. 94°–95° and of the *ethyl ester* m.p. 65·5°. The *copper salt* $Cu(C_3H_6NO_2)_2,6H_2O$ has the properties of an ordinary copper salt, and not those of a cuprammonium derivative (Callegari, Gazz. chim. ital. 1906, 36, ii. 63).

β-Alanine does not occur naturally in the body; when administered with food it causes an increase in the urinary nitrogen, but it is apparently changed with more difficulty than α-alanine, as the increased nitrogen excretion is not observed until the second day (Abderhalden and Schittenhelm, Zeitsch. physiol. Chem. 1907, 51, 323). M. A. W.

ALANT CAMPHOR *v.* Camphor.

ALANT ROOT. The root of *Inula helenium* is said to contain antiseptic principles, efficacious against tuberculosis bacilli. By distilling the root with water, *helenin*, *alantic acid*, and *alantol* (alant camphor) are obtained. *Alantic acid* $C_{15}H_{22}O_3$ crystallises from alcohol in white crystals, m.p. 91°; and on heating it forms the *anhydride* $C_{15}H_{20}O_2$. Both acid and anhydride are insol. in water, sol. in alcohol or fatty oils; form sol. salts with alkalis. *Alantol* is an aromatic liquid, b.p. 200° (Marpmann, Pharm. Zent. 8, 122; J. Soc. Chem. Ind. 1887, 520).

ALBARGIN. Gelatose-silver: a colloidal preparation of silver.

ALBASPIDIN *v.* Filix mas.

ALBERTITE. A jet-black mineral substance resembling asphalt, discovered in 1849, at Hillsborough, Albert co., New Brunswick. Used in the United States for the production of oil and coke. The yield per ton is said to be 100 gallons of crude oil, and 14,500 cubic feet of illuminating gas, whilst a residue of good coke remains in the retorts. Albertite has been found at Strathpeffer, Ross-shire; it contains 62 p.c. volatile matter, 37 p.c. fixed carbon, and 0·60 p.c. water. Its ultimate composition is 79·75 p.c. carbon, 8·12 p.c. hydrogen, 1·63 nitrogen, and 10·30 oxygen (Morrison, Min. Mag. 6, 101; Chem. Soc. Abstr. 50, 311).

ALBITE *v.* Felspar.

ALBUM GRÆCUM. A term formerly used for the excrement of dogs. It was at one time supposed to have medicinal properties, but is now used only for tanning, as skins treated with it, after the removal of the hair and previous to tanning, preserve their softness. It consists mainly of phosphate of lime. Fowls' dung is said by tanners to answer the purpose better.

ALBUMINOIDS and ALBUMINS *v.* Proteins.

ALCOHOL (Ethylic or Vinous) C_2H_6O, the active principle of ordinary intoxicating liquors. Contrary to the usual statement, alcohol was unknown to the Arabian chemists. The process of distillation was also unknown in Asia. The discovery of alcohol probably took place in Italy. It is first mentioned in an Italian work of the ninth or tenth century (Lippman).

Ethyl alcohol occurs, as esters, in many plants. and in various lichens; and is formed by distilling certain plants and fruits with water, probably by hydrolysis of the esters, or by the action of moulds and bacteria on carbohydrates.

Preparation.—Synthetically from its elements thus:—By passing an electric arc between carbon poles in an atmosphere of hydrogen, acetylene (C_2H_2) is produced, which, in the presence of nascent hydrogen, becomes ethylene (C_2H_4). Ethylene by protracted shaking with sulphuric acid is converted into sulphovinic acid, which, being distilled in presence of water, produces alcohol.

Alcohol is, for practical purposes, usually prepared by dehydrating the products of the distillation of fermented liquids. Up to 1796 the strongest spirit known contained not less than 5 p.c. of water. Lowitz appears to have been the first to prepare it in an approximately anhydrous condition. His process consisted in first increasing the strength of rectified spirit by adding to it potassium carbonate, and after decanting from this, distilling very slowly in presence of a further quantity of dry potassium carbonate. Richter used, instead of potassium carbonate, hot calcium chloride (Crell's Ann. 2, 211). Drinkwater first digested with dry potassium carbonate for twenty-four hours; decanted the strong spirit thus produced, digested with as much fresh-burnt quicklime as was sufficient to absorb the whole of the alcohol, and afterwards distilled in a water-bath at a temperature of 82·2°. The product of this distillation, which was found to have a specific gravity of 0·7946 at 15·6°, was returned to the retort, and a fresh quantity of dry pulverised quicklime added to it, after which it was allowed to digest for a week at a temperature of 15·6°. It was then again slowly distilled and the specific gravity of the product found to be 0·7944 at 15·6°. This was digested at a temperature of 54·4° with hot quicklime, and distilled out of contact with the air at a temperature of 81·1° to 82·2°, and the specific gravity of the product, which was taken as absolute alcohol, found to be 0·793811 at 15·6°/15·6°.

Squibb followed the process of Drinkwater, distilling in a partial vacuum of 380 to 630 mm. The alcohol thus prepared had a specific gravity of 0·79350. The difference between this specific gravity and that found by Drinkwater represents one tenth p.c. of alcohol. Mendeléeff's observations (Pogg. 138, 103, 230) practically confirm those of Drinkwater and Fownes.

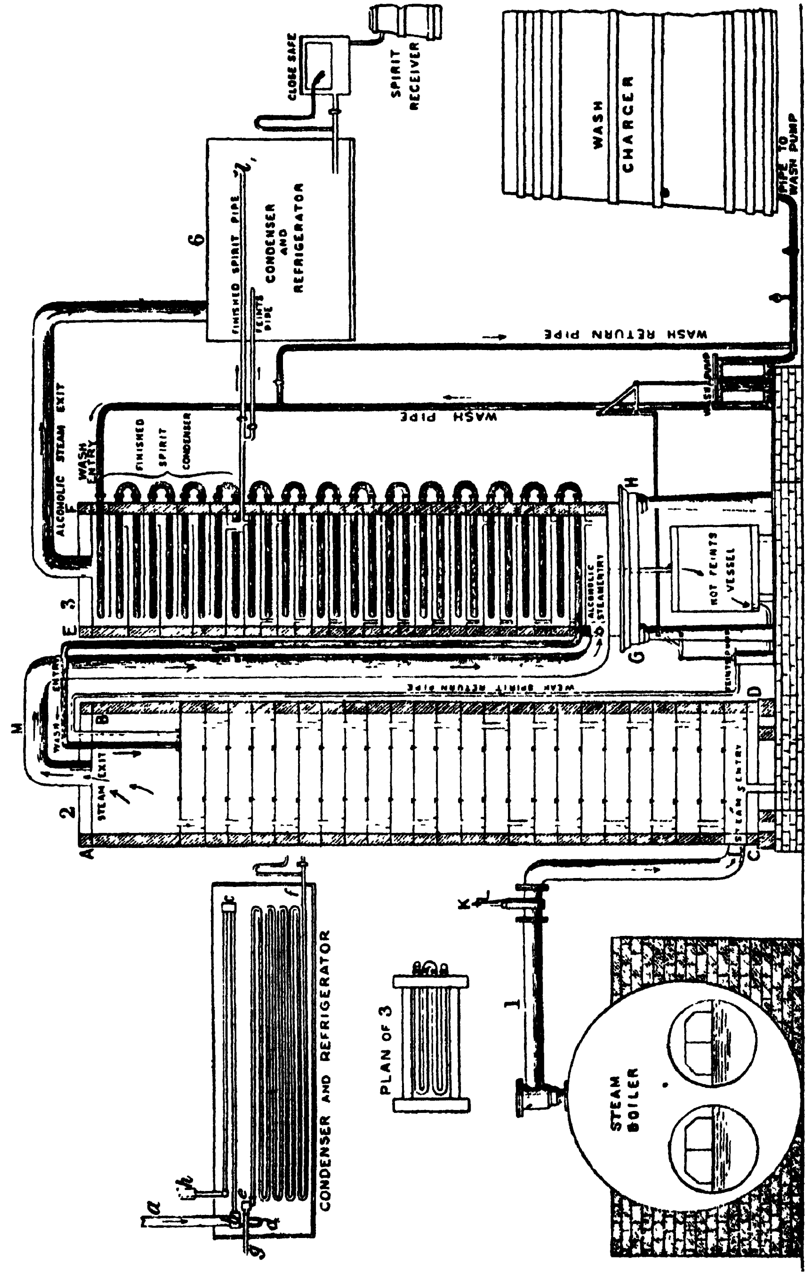
Metallic calcium, free from calcium nitride, may be used to dehydrate alcohol. The calcium should be in shavings, washed with dry carbon tetrachloride to remove traces of petroleum, in the proportion of 20 grams of cleaned and sieved shavings to every litre of alcohol. In order to remove ammonia from the distillate (due to possible traces of calcium nitride) a few centigrams of alizarin are dissolved in a litre of the distilled alcohol together with 0·5 gram of dry tartaric acid dissolved in 10 c.c. of the alcohol. The tartaric acid solution is slowly added to the alcohol coloured by the alizarin until the reddish-blue colour changes to yellow, when the whole is again distilled.

Manufacture.—The first process in the manufacture of spirit is one of brewing, and in general principles it does not differ from that employed in making beer. The brewer, as well as the distiller, endeavours to treat his materials in such a way as to extract from them the greatest amount of fermentable matters. The brewer of beer, however, does not desire to convert all the matter he extracts into spirit, and he brews at such gravities as his customers require. The distiller desires to convert as much as possible of the matter he has extracted from his materials into spirit; he therefore produces a wort containing more maltose and less dextrinous matter than the brewer of beer. He has also an advantage over the brewer in being able to choose the gravities which he knows by experience will produce the best results. It has been found that for distillers' purposes it is advisable to keep the specific gravity of the wort when set for fermentation below 1040. The principle of low temperatures when the diastase is acting in the mash tun appears to be fully recognised, 60° to 63° being generally adopted, and it is understood that the higher the temperature at which the worts are set for fermentation, the greater is the amount of fusel oil in the spirit. The distiller has, therefore, to choose the lowest temperature at which a healthy fermentation can be started, and this is found to range between 23° and 25°. He cannot be too careful as to the purity of the yeast, for not only has he to run the risk of acetic and other ferments being introduced into the wort, involving loss of alcohol, but to provide against the presence of aldehyde, which is objectionable in the spirit. It is found in practice that it is always more prone to appear in hot weather, when the difficulty of keeping the yeast from decomposition is greatest, and as yeast always contains some spirit in a dilute form it is not improbable that the aldehyde is frequently a product of the oxidation of this spirit. Acrolein (probably derived from glycerol) ammonia, and sulphur in organic combination are occasionally found in small quantities in crude spirit.

The materials used in the manufacture of alcohol in the United Kingdom are chiefly malt, maize, rice, sago, tapioca, barley, rye, oats, sugar, and molasses, but occasionally dates and locust beans have been employed. At the present time *maize* constitutes fully 75 p.c. of the grain used. In Scotland the smaller distillers use malt only, and the spirit they produce under the name of Highland, Campbeltown, or Islay Whiskey, Glenlivet, Lochnagar, &c., has imparted to it a flavour derived partly from the peat used in drying the malt. The process of manufacture consists in distilling the fermented wort—then called wash—in a common still, collecting the distillate, which is weak spirit contaminated with fusel oil, and is called 'low wines,' and redistilling. The spirit which passes over in the middle of the redistillation is that which is used for consumption. It contains from 60·8 to 76·7 p.c. of alcohol by weight (20 overproof to 45 overproof), but is generally diluted by the addition of water to 55·4 p.c. of alcohol by weight (11 overproof) before being sent into consumption or placed in bond. Irish whiskey differs from Scotch chiefly in the absence of peat flavour. The materials used in its manufacture are, with one or two exceptions, a mixture of malt and grain, the proportion of malt being, however, greater than in English distilleries. It is generally bonded at 25 overproof (64 p.c. of alcohol by weight).

We have hitherto dealt with the spirit manufactured in 'Common' or 'Pot' stills, or in other words by boiling the wash, condensing the steam thus produced, reboiling the product and recondensing. But by far the greater quantity of the alcohol of commerce is produced by the Coffey still, in which the alcoholic vapour produced is deprived of water as the process continues until a spirit is formed of much greater purity than that manufactured by the old method. The annexed illustration represents a Coffey's distilling apparatus, the left-hand column being called the *analyser*, the right hand one the *rectifier*. The first operation is to fill both columns with steam. This is accomplished by introducing it under pressure from the boiler at C, whence it ascends within the analyser, passing by the pipe M into the bottom of the rectifier. When a proper temperature has been attained, the wash is pumped from the wash charger by a pipe which enters the top of the rectifier. This pipe is only shown sectionally in the sketch after entering the column, but it is continuous, and the wash passes slowly through it, becoming warmer, owing to the pipe being in contact with the steam. When it has reached the bottom of the rectifier it is not far from the boiling-point. It will be seen that the pipe then ascends, and finally delivers the wash into the top of the analyser. The lines across the analyser represent plates of perforated copper, and in connection with each is a tube which projects about an inch and a half above the plate, and dips into a shallow vessel placed on that next beneath. The wash on entering falls on the first plate, but on reaching a depth of an inch and a half passes through the tube to the second one. In the mean time the steam produces ebullition in the contents of the plates, and carries away with it the alcoholic vapour through the steam exit pipe, so that by the time the wash has reached the bottom of the column it has been deprived of its alcohol. The alcoholic vapour passes by the pipe M into the bottom of the rectifier, which like the analyser contains plates and metal tubes, and where a process of gradual cooling takes place by the action of the pipe carrying the cold wash. Fusel oil vapour, condensing at a higher temperature than alcohol, is the first to assume the liquid form, and contaminated with spirit passes into the hot 'feints' receiver. The vapour containing alcohol continues to ascend, meeting with portions that have condensed, and are undergoing the process of rectification. It will be seen that the upper part of the apparatus is marked off in the sketch as finished-spirit condenser. It is so called because all that condenses within its area, instead of returning towards the bottom of the apparatus to be rectified, passes by the finished-spirit pipe or feints pipe into the receivers. At the top of the apparatus is a pipe marked 'alcoholic steam exit,' which carries away most of the aldehyde as well as spirit vapour which under special circumstances may not have been condensed before reaching that point.

The English distillers confine themselves almost exclusively to this apparatus, brewing for the most part from a mixture of grain and malt. In addition to Coffey's still, various forms of rectifying stills are in use to meet special requirements, *e.g.* the production of a purer though not stronger spirit than that obtainable from the Coffey still for the purpose of compounders and certain manufacturing processes, and apparatus having for their object (in consequence of the increasing demand for fusel oil) the recovery of the maximum amount of this by-product, which indeed is now considerably more valuable than the spirit itself. The spirit produced does not to any large extent go into consumption as whiskey, the want of flavour being an objection in regard to the better qualities. Large quantities are transferred to the rectifiers, who redistil them with various



flavouring ingredients, producing gin, British brandy, British rum, and the various cordials, A portion, after being redistilled from potassium carbonate, or filtered through charcoal, is used in the arts and in medicine under the names of rectified spirit and spirits of wine. The British Pharmacopœia (1914) requires rectified spirit to be of a specific gravity of 0·8337 at 15·6°/15·6°, equal to 85·68 p.c. of alcohol by weight. The Pharmacopœia of the United States fixes it at 0·820, equal to 91 p.c., which is about the strength it comes from Coffey's apparatus. The four official (B.P.) diluted alcohols obtained by mixing 90 p.c. alcohol (*Spiritus rectificatus*) with distilled water contain, respectively, 70, 60, 45, and 20 p.c. of alcohol by volume.

They are prepared as follows:—

1. *Seventy per cent. Spirit.*—Sp.gr. 0·8899. Mix 310·5 c.c. of distilled water with 1 litre of 90 p.c. alcohol. Or dilute 777·8 c.c. of 90 p.c. alcohol with water so as to make 1 litre at 15·5°.

2. *Sixty per cent. Spirit.*—Sp.gr. 0·9134. Mix 536·5 c.c. of distilled water with 1 litre of 90 p.c. alcohol. Or dilute 666·7 c.c. of 90 p.c. alcohol with water so as to make 1 litre at 15·5°.

3. *Forty-five per cent. Spirit.*—Sp.gr. 0·9435. Mix 1053·4 c.c. of distilled water with 1 litre of 90 p.c. alcohol. Or dilute 500·0 c.c. of 90 p.c. alcohol with water to the bulk of 1 litre at 15·5°.

4. *Twenty per cent. Spirit.*—Sp.gr. 0·9760. Mix 3558·0 c.c. of distilled water with 1 litre of 90 p.c. alcohol. Or dilute 222·2 c.c. of 90 p.c. alcohol with water to the bulk of 1 litre at 15°.

Attempts have been made, especially in America, to produce alcohol from wood, by the Classen process, or by some modification of it. This process consists in converting the cellulose of the wood or some portion of it into dextrose and other sugars by treatment with dilute acid under pressure, and, after neutralising the acid, fermenting the sugar with yeast, and separating the alcohol by distillation. The yield is about 21 gallons of 95 p.c. alcohol per ton of wood, sawdust or pine wood waste being usually employed, the output being upwards of 2000–2500 gallons *per diem*. The method has not been commercially successful in this country, and is carried on only to a limited extent, and under exceptional conditions, in the United States (J. Ind. Eng. Chem. 1911, 3, 439; 1915, 7, 920; J. Soc. Chem. Ind. 1912, 31, 513; 1917, 36, 532; 1918, 37, 131; Chem. Tr. J. 1918, 63, 103; Zeitsch. angew. Chem. 1913, 26, 786; J. pr. Chem. 1915, 91, 358; Chem. and Metall. Eng. 1918, 19, 552).

Some considerable quantity of alcohol is, however, obtained from the waste liquors formed in the manufacture of wood pulp by the sulphite process. This liquor contains from 1 to 2 p.c. of sugars, which, after neutralisation, or removal of the sulphur dioxide, can be fermented and the alcohol recovered by distillation. The industry is established in Norway, Sweden, Germany, Switzerland, and on the American continent. The yield of alcohol is said to be about 1 p.c. or rather more, of the sulphite waste liquor. The spirit obtained contains methyl alcohol, and is therefore unsuitable for potable purposes; but it can, of course, be employed as motor fuel, and for other uses where a denatured spirit is applicable (Johnsen, J. Soc. Chem. Ind. 1918, 37, 131T).

The synthetic production of alcohol from acetylene, produced from calcium carbide, was largely developed in Germany during the war. The methods employed consist either in transforming the acetylene into ethylene and thence into alcohol by treatment with oil of vitriol and water by a process first discovered by Hennell in 1828; or by converting the acetylene into aldehyde in presence of a catalyst, such as a mercury salt, and then reducing the aldehyde to alcohol by passing its vapour, mixed with hydrogen, over finely divided nickel, at a particular temperature.

For descriptions of the various forms of potable spirit—brandy, rum, whisky, gin, &c.—*see* the special articles on these subjects.

Properties.—In the dehydrated condition ethyl alcohol is a colourless liquid, having a specific gravity of 0·791 at 20°/20° (Lowitz, Crell's Ann. 1796, 1, 1), 0·7938 at 15·6°/15·6° (Fownes, Phil. Trans. 1847, 249), 0·793811 at 15·6°/15·6° (Drinkwater, Phil. Mag. Feby. 1848), 0·79350 at 15·6°/15·6°, 0·79367 at 15°/4° (Mendeléeff, Pogg. 138, 230), (Squibb, Ephemeris, 1884–5, and Pharm. J. [3] 16, 147–148), 0·7851 at 25°/4° (Winkler, Kailan, Osborne, McKelvy, and Bearce, J. Washington Acad. Sci. 1912, 2, 95), 0·7936 at 15°/4° (Schoorl and Regenbogen, Proc. K. Akad. Wetensch. Amsterdam, 1918, 20, 831), 0·80627 at 0°/4° (Young, Klason, and Norlin, Merriman). It boils at 78·4° under a pressure of 760 mm. (Kopp, Annalen, 92, 9), 78·3° (Young and Merriman), and solidifies at −130·5° (Wroblewski and Olsewski, Compt. rend. 96, 1140 and 1125), –112·3° (Ladenburg and Krugel, Ber. 1899, 32, 1818). It is inflammable, the combustion evolving great heat but little light, and producing carbon dioxide and water. It acts as a caustic irritant in contact with the tissues of the body, owing probably to the energy with which it draws moisture from the surface. It possesses a specific heat of 0·6120 at temperatures between 16° and 40·5° (Schüller, P. Erg. 5, 116–192). Its index of refraction for $H\beta$=1·3667 (Brühl), and its critical temperature 243·6° at 48·9 m. At this point 1 gram occupies 3·5 c.c. (Ramsay and Young, Proc. Roy. Soc. 38, 329).

VAPOUR PRESSURE OF ETHYL ALCOHOL.
(Merriman, Trans. Chem. Soc. 1913, 103, 632.)

°	Pressure in mm.	°	Pressure in mm.
0	12·0	18	38·7
1	12·9	19	41·2
2	13·9	20	43·8
3	14·9	21	46·5
4	15·9	22	49·4
5	17·0	23	52·4
6	18·2	24	55·6
7	19·4	25	59·0
8	20·7	30	78·6
9	22·1	40	134·9
10	23·5	50	222·2
11	25·1	60	352·7
12	26·7	70	542·5
13	28·4	80	812·7
14	30·3	90	1187·0
15	32·2	100	1694·0
16	34·3	105	2007·0
17	36·4		

The viscosity of ethyl alcohol at various temperatures has been measured by Thorpe and Rodger (Phil. Trans. 1894, 185, II, 533), with the results shown in the annexed table:—

Temperatures. °	η	Temperatures. °	η
7·16	0·015328	42·34	0·007875
13·23	0·013573	49·37	0·007047
19·22	0·012094	55·57	0·006354
25·24	0·010792	61·07	0·005815
31·89	0·009560	67·55	0·005253
37·51	0·008644	73·57	0·004764

The electric conductivity of alcohol and of its aqueous solutions has been determined at 15°, by Doroschewsky and Roschdestvensky (J. Russ. Phys. Chem. Soc. 1908, 40, 887; J. Soc. Chem. Ind. 1909, 28, 853).

Ethyl alcohol is hygroscopic and is miscible with water in all proportions. On adding water to anhydrous alcohol a considerable development of heat occurs owing to the contraction in the resultant volume. The maximum contraction is found by mixing 48 vols. of water with 52 vols. of anhydrous alcohol, measured at 15·56°.

H. T. Brown (Analyst, 1915, 40, 379) has shown from the alcoholometric tables published by Thorpe that in the case of mixtures of very dilute alcohol and water there is a slight expansion instead of contraction.

Commercial 'absolute' alcohol usually contains about 1 p.c. to 1·5 p.c. of water. In the B.P. (1914) 'absolute' alcohol is defined as 'ethyl hydroxide C_2H_5OH, with not more than 1 p.c. by weight of water; sp.gr. from 0·794 (equivalent to 99·95 p.c. of ethyl hydroxide by volume and by weight) to 0·7969 (equivalent to 99·4 p.c. of ethyl hydroxide by volume or 99 p.c. by weight). Anhydrous copper sulphate shaken occasionally during two or three hours in a well-closed vessel with about fifty times its weight of absolute alcohol does not assume a decidedly blue colour (absence of excess of water).'

Absolutely anhydrous alcohol should give no cloudiness when mixed with benzene, and no pink colouration when shaken with a crystal of potassium permanganate, and no turbidity or evolution of gas (acetylene) in contact with calcium carbide. Anhydrous alcohol added to a fragment of anthraquinone and sodium amalgam acquires a green colour; if a trace of water be present the colour becomes red (Claus, Ber. 10, 927).

Ethyl alcohol is readily detected by the formation of *ethyl acetate* on adding sodium acetate and a few drops of acetic acid to the liquid to be tested, together with an equal volume of strong sulphuric acid, and heating the mixture, when the characteristic smell of ethyl acetate is produced. A less characteristic reaction is the formation of *iodoform* when the liquid is mixed with a few drops of a solution of iodine and warmed and the colour of the iodine destroyed by a solution of sodium carbonate or hydroxide. If *benzoyl chloride* be shaken with the liquid, it forms ethyl benzoate; on warming the decanted solution with a solution of caustic potash the ethyl benzoate is recognised by its odour. Other tests are the formation of *aldehyde* by the action of a mixture of potassium dichromate and sulphuric acid, recognised by its smell and its behaviour with Schiff's reagent; the formation of *dinitrophenetole* (Blanksma, Chem. Weebklad, 1914, 11, 26); *phthalic ester* (Reid, J. Amer. Chem. Soc. 1917, 39, 1249).

According to Pasteur very small traces of ethyl alcohol, especially in fermented liquids, may be detected on distilling the aqueous liquid suspected to contain it by observing the formation of the striæ, or 'tears' produced by the condensation of the first few drops of the distillate. A few c.c. of the liquid to be tested are placed in a wide test tube fitted with a cork and a long glass tube. The liquid, which should contain a spiral of copper or platinum wire, or a few fragments of pumice, to ensure regular ebullition, is heated by a small flame and the formation of the 'tears' in the long tube noticed. With care as little as 0·001 p.c. of alcohol can in this way be detected.

Alcohol forms ethoxides with sodium and potassium, and unstable compounds with certain crystalline salts, *e.g.* zinc chloride, the latter called alcoholates. Subjected to the action of a limited supply of oxygen, it is converted into aldehyde (C_2H_4O), which, by further oxidation, becomes acetic acid ($C_2H_4O_2$). Distilled with chloride of lime, it forms chloroform ($CHCl_3$). With sulphuric acid at a temperature not exceeding 145° it yields ether ($C_4H_{10}O$). With twice its bulk of sulphuric acid it gives ethylene (C_2H_4). With excess of dry chlorine gas it produces chloral (C_2HCl_3O).

Uses.—In addition to its use as a beverage, spirit is employed as a solvent for many of the drugs required in medicine, and diluted to the standard of British proof—that is, to the specific gravity of 0·91976 at 15·6°, representing 49·28 p.c. by weight of Drinkwater and Fownes alcohol—it forms part of a large proportion of the tinctures of the Materia Medica. It is also used largely as a solvent for essential oils, in preparing perfumes and essences, and ether and other ethyl derivatives are manufactured from it.

Methylated spirit. In 1853 a strong representation was made to the Government to allow the use of alcohol duty free in the arts and manufacturing processes in which it was required, and after careful inquiry the Board of Inland Revenue in 1855 decided to sanction, under certain restrictions, a mixture of nine parts of spirits of wine and one part of methyl alcohol (wood naphtha) free of duty under the name of *methylated spirits.* In 1861 the permission was extended to all other purposes except consumption as a beverage or as a medicine. The reasons for selecting wood naphtha were that whilst it would be least likely to interfere in any of the processes for which alcohol was required—especially as a solvent—it would be very difficult to separate from the alcohol when once mixed. The principal restriction on the use of methylated spirit is that it shall only be kept by authorised persons and in authorised premises.

In 1891 it was found necessary (owing to the possibility of methylated spirit being sufficiently purified to render it fit for potable purposes, and the growing practice of drinking even the unpurified methylated spirit by the poorer classes in some of the larger cities) to again restrict the use of methylated spirit made as above described (*i.e.* 'ordinary methylated spirit') to manufacturers only, and, even then, subject to revenue restrictions, and to prescribe the addition of a further denaturant to methylated spirit intended for general purposes. This denaturant consists of mineral naphtha (petroleum), and the mixture, known as '*mineralised*' methylated spirit, may be sold by licensed retailers to the general public for any purpose to which it is applicable, as lighting, heating, cleansing, or mixing with paints, varnishes, &c.

It was found, however, that 'ordinary' methylated spirit was not universally applicable to manufacturing processes requiring the use of alcohol, and accordingly, in 1902, the Commissioners of Inland Revenue, under powers conferred upon them by the Spirits Act of 1880 and the Finance Act of 1902, authorised the use of duty-free alcohol denatured with substances other than wood-naphtha in certain manufacturing operations and subject to special conditions.

As the result of an inquiry by a Departmental Committee, in 1904–5, the amount of wood-naphtha to be used as a denaturant for 'ordinary' methylated spirit used for industrial purposes was reduced from 10 to 5 p.c. of the mixture. This is described as '*industrial*' *methylated spirit.*

At the present time (1920), there are, therefore, two descriptions of methylated spirit officially recognised in the United Kingdom, viz.:

(*a*) *Mineralised methylated spirit* as sold by licensed retailers for general use (except for the preparation of beverages or medicine), and containing not less than 10 p.c. by volume of approved wood-naphtha, and, in addition, not less than 0·375 p.c. of approved mineral naphtha (petroleum of specific gravity not less than 0·800).

(*b*) *Industrial methylated spirit,* intended for use in manufacturing processes, and sold only by methylators to persons authorised to receive this kind of spirit. This must contain not less than 5 p.c. of approved wood-naphtha or other substance or combination of substances approved by the Commissioners of Customs and Excise.

The wood-naphtha must be sufficiently impure to make the methylated spirits so nauseous as to render them incapable of being used as a beverage or of being mixed with potable spirits without rendering them unfit for human consumption. It must contain not less than 72 p.c. by volume of methyl alcohol, and not more than 12 grams per 100 c.c. of aldehydes, acetone, and higher ketones, estimated as acetone by Messinger's iodoform process, nor more than 3 grams of esters estimated as methyl acetate by hydrolysis; not more than 30 c.c. of naphtha shall be required to decolourise an aqueous solution containing 0·5 gram of bromine, and 5 c.c. at least of deci-normal acid shall be required to neutralise 25 c.c. of the spirit when methyl orange is used as indicator.

The wood-naphtha which is now used by methylators is fairly uniform in character as regards its content of methyl alcohol, and it is by the recognition of this alcohol that the presence of methylated spirits is usually detected. Acetone is present in much more varying quantities, whilst unsaturated alcohols, compound ethers, and nitrogenous basic substances are present in too small and varying proportions to afford suitable means for detecting methylated spirits in mixtures.

The most satisfactory methods for detecting methyl alcohol in presence of ethyl alcohol depend either on differences in the physical properties of the alcohols themselves, or on differences in the chemical behaviour of their derivatives or products of oxidation, but of these, few are capable of indicating with certainty the presence of less than 1 p.c. of methyl alcohol.

Of the methods which have hitherto been devised for this purpose, none can compare, as regards the certainty of the conclusions which may be drawn from the results, with that of Riche and Bardy, which depends on the ultimate formation of methylaniline violet and its deposition on wool (Compt. rend. 1875, 1976). As a preliminary test, and one which may with advantage be incorporated in the Riche and Bardy process, the following will be found to be useful. About 10 c.c. of the strong spirit—freed, if necessary, from essential oils, &c., by the salt-petroleum method and fractionated from potassium carbonate (*v.* ALCOHOLMETRY)—are placed with 30 grains of powdered iodine in a small round-bottomed flask which can be readily connected with a condenser. Two grams of amorphous phosphorus are added and the resulting alkyl iodides distilled and collected under water in a small separator. When from 10 to 12 c.c. have been collected, the iodides are washed with water, decolourised with dilute potash, and drawn off from the aqueous layer into a flask containing a little freshly heated potassium carbonate. After remaining an hour or so with occasional shaking, the potassium carbonate is removed by filtration, and the boiling-point of the iodides carefully determined. Ordinary ethyl alcohol yields an iodide which has a constant boiling-point of 72°. When methyl alcohol is present in the spirit, the initial boiling-point of the iodides is lower and a portion distils below this temperature. By noting the temperature at which the first drop of distilled iodides falls into the condenser and receiver respectively, the presence of relatively small quantities of methyl alcohol can be detected. The results (see table in next col.) obtained with synthetic mixtures indicate the delicacy of the method.

In doubtful cases, or when the initial boiling-point is below 70°, the first fraction of 3 c.c. of distilled iodides is digested with an equal volume of aniline at a moderate temperature, and the Riche and Bardy method proceeded with. After standing one hour, hot water is added to the crystalline mass, and the mixture boiled for some minutes, 25 c.c. of strong potash solution are then added, and the liberated aniline oil washed with water; 1 c.c. of this oil is intimately mixed with 10 grams of a mixture consisting of 100 grams of dry quartz sand, 3 grams of cupric nitrate, and 2 grams of common salt, and the mixture introduced into a wide tube and heated for some hours at 90°–100°. The product is exhausted with warm alcohol and the extract filtered and made up to a volume of 100 c.c.

If the sample of spirit contained ethyl alcohol only, the colour of the liquid will be red, but in the presence of 1 p.c. of methyl alcohol it has a distinct violet shade, whilst in the presence of 2 p.c. the violet is very decided, and becomes more so as the proportion of methyl alcohol increases. 5 c.c. of the alcoholic extract are then mixed with water to a volume of 100 c.c., and 2 c.c. of this dye diluted with water to about 400 c.c. The mixture is now heated to a temperature not exceeding 75°, and from two to three feet of Berlin wool, previously freed from grease by treatment with hot dilute potash, immersed in it for 30 minutes.

Percentage of methyl alcohol by volume in the mixture of alcohols	Temperature at which the first drop of iodides falls into the condenser	Volume of distillate obtained below 72° from 10 c.c. of iodides
		c.c.
Nil	70°	Nil
0·38	69°	0·2
0·94	65°	0·8
1·86	63°	2·2
2·77	62°	4·0
3·66	60°	5·0
4·55	58°	6·0
5·42	57°	6·2
6·26	56°	6·4
7·10	55°	6·5
10·00	52°	7·5

Pure ethyl alcohol under these conditions will not produce a dye, and the wool after washing and drying remains practically white. If, however, methyl alcohol was originally present, the fibre will be violet, the tint becoming more intense and increasing in depth according to the quantity present. Riche and Bardy recommend that 5 c.c. of the above diluted dye should be taken instead of 2 c.c. as here described, but although by this means a more intense dye is obtained when methyl alcohol is present, it is found that an appreciable dye, although not of the same colour, is deposited when pure ethyl alcohol has been operated with, and this may lead to confusion. For purposes of comparison it is therefore advisable to operate concurrently with a sample of rectified spirits.

If it be desired to estimate the proportion of methyl alcohol or methylated spirits in a sample, the method of Thorpe and Holmes may be employed. This method depends on the complete oxidation of methyl alcohol to carbon dioxide by means of chromic acid mixture, rectified spirits under the same conditions yielding only a small quantity of carbon dioxide equivalent to 0·01 gram for each gram of ethyl alcohol present (Chem. Soc. Trans. 1904, 1).

As a result of many experiments it has been proved that unless the boiling-point of the iodides is abnormal, no dye is obtained by the Riche and Bardy method, nor does the yield of carbon dioxide on oxidation exceed the limits given above for rectified spirits, but in all cases in which a dye is obtained a proportional excess of carbon dioxide is also obtained.

In other countries there are, as a rule, classes of denatured alcohol corresponding more or less with those authorised in the United Kingdom, *i.e.* spirit for general use so completely denatured as to be deemed undrinkable, and spirit not absolutely denatured and intended for use by responsible manufacturers subject to a more or less strict revenue control.

Wood-naphtha is the denaturant most in favour for spirit intended for general use, the nauseous character of the methylated spirit being sometimes intensified by the addition of such substances as pyridine bases, benzine, &c.

In *France*, spirit for general use contains one-eleventh of its volume of officially approved wood-naphtha, with an addition (when used for lighting and heating purposes) of 0·5 p.c. of heavy benzine distilling between 150° and 200° and 4 p.c. of gum resin for 'finish.'

In *Germany*, the official formula is 2 p.c. of wood naphtha, 0·5 p.c. of pyridine bases, and (optionally) 0·125 p.c. of rosemary oil. Spirit intended for motor cars, and internal combustion engines is denatured by adding 1 p.c. of wood-naphtha, 0·25 p.c. of pyridine bases, 0·25 p.c. of a solution of methyl violet dye, and from 2 to 20 p.c. of benzol to the pure spirit.

In the *United States of America*, 10 p.c. of approved methyl alcohol and 0·5 p.c. of benzene is prescribed to be added to spirit denatured for general use.

In *Belgium*, specific denaturants are prescribed for each of the principal manufacturers, and this practice obtains in certain other countries, as Germany, France, Switzerland, America, and the United Kingdom, when it can be shown that ordinary methylated spirit is unsuitable. In such cases the denaturants are naturally very varied in character, being specially adapted to the particular necessities of each manufacturer.

(Minutes of Evidence and Report of the Department Committee on Industrial Alcohol, 1905; Herrick, Denatured or Industrial Alcohol.)

ALCOHOLOMETRY is the term applied to any process for estimating the amount of alcohol in a spirituous liquid. In simple mixtures of alcohol and water a determination of specific gravity at a standard temperature affords an accurate index of alcoholic content, and it is by taking advantage of this fact that the assay of spirit for revenue and commercial purposes is usually carried out.

When alcohol and water are mixed together the volume of the mixture is invariably less than the sum of the initial volumes, and the degree of contraction varies with the proportion of alcohol present. In countries in which the revenue from spirit is of great importance it has therefore been found necessary to ascertain by experiment the specific gravities of mixtures of alcohol and water in all proportions and at various temperatures. These experiments have in general been carried out at the request of the Governments interested, and the results are embodied in tables associated with the names of those entrusted with the investigations.

In 1794 Sir Charles Blagden and Mr. Gilpin completed an extensive series of experiments, undertaken at the request of the British Government (Phil. Trans. 1790–1794), the results of which have since served as the basis of systems of alcoholometry in this and other countries. At that time anhydrous alcohol had not been prepared, Blagden and Gilpin's tables having reference to spirit of a sp. gr. 0·825 at 15·6°/15·6° (60°/60°F.). Tralles, in 1811, conducted a like investigation for the Prussian Government (Gilb. Ann. 1811), and adopted 0·7946 as the specific gravity of alcohol at 15·6°/15·6°. He incidentally confirmed the general accuracy of the results of Blagden and Gilpin, and constructed tablet of spirit-strengths which for upwards of sixty years formed the basis of German alcoholometry. Similar researches were undertaken by Gay-Lussac (Paris, 1824), McCulloch (Washington, 1848), Baumhauer (Amsterdam, 1860), Mendeléeff (St. Petersburg, 1865), and more recently by the Kaiserliche Normal Eichungs Kommission (Berlin, 1889), the several results of which have from time to time been incorporated in the systems of alcoholometry adopted by the respective Governments. The unofficial investigations, of Fownes (Phil. Trans. 1847), Drinkwater (Chem. Soc. Mem. 848), and Squibb (Ephemeris, 1884), are likewise entitled to consideration.

Drinkwater prepared alcohol of a specific gravity 0·79381 at 15·6°/15·6° (in air), whilst Squibb obtained it as low as 0·7935, but this result lacks confirmation.

The work of Mendeléeff for the Russian Government admittedly constitutes the most

Specific gravity in air at $\frac{15{\cdot}6^\circ}{15{\cdot}6^\circ}$	Percentage of alcohol		Percentage of fiscal proof spirit
	by weight	by volume at 15·6°	
0·79359	100·00	100·00	175·35
0·794	99·87	99·92	175·21
0·796	99·22	99·52	174·52
0·798	98·57	99·12	173·80
0·800	97·91	98·70	173·07
0·802	97·25	98·28	172·33
0·804	96·57	97·84	171·56
0·806	95·89	97·39	170·77
0·808	95·20	96·93	169·96
0·810	94·50	96·45	169·13
0·812	93·80	95·97	168·28
0·814	93·08	95·47	167·41
0·816	92·36	94·97	166·51
0·818	91·63	94·45	165·60
0·820	90·90	93·92	164·67
0·822	90·16	93·38	163·72
0·824	89·41	92·83	162·75
0·826	88·65	92·26	161·76
0·828	87·88	91·69	160·75
0·830	87·11	91·11	159·73
0·832	86·34	90·52	158·69
0·834	85·56	89·91	157·63
0·836	84·78	89·30	156·56
0·838	83·99	88·68	155·47
0·840	83·20	88·06	154·37
0·842	82·40	87·42	153·25
0·844	81·60	86·77	152·12
0·846	80·79	86·12	150·97
0·848	79·98	85·46	149·80
0·850	79·17	84·78	148·62
0·852	78·35	84·11	147·43
0·854	77·53	83·42	146·23
0·856	76·71	82·73	145·01
0·858	75·88	82·03	143·78
0·860	75·05	81·32	142·54
0·862	74·22	80·61	141·28
0·864	73·39	79·89	140·02
0·866	72·55	79·16	138·74
0·868	71·72	78·43	137·46
0·870	70·88	77·69	136·16
0·872	70·04	76·94	134·84
0·874	69·19	76·19	133·53
0·876	68·35	75·44	132·19
0·878	67·51	74·68	130·86
0·880	66·66	73·91	129·50
0·882	65·81	73·13	128·14
0·884	64·96	72·34	126·77
0·886	64·10	71·55	125·37
0·888	63·24	70·75	123·97
0·890	62·38	69·95	122·56
0·892	61·52	69·14	121·14
0·894	60·66	68·33	119·70
0·896	59·80	67·50	118·26
0·898	58·93	66·67	116·81
0·900	58·06	65·83	115·33
0·902	57·18	64·98	113·84
0·904	56·31	64·13	112·35
0·906	55·42	63·26	110·82
0·908	54·54	62·39	109·29
0·910	53·65	61·51	107·74
0·912	52·77	60·63	106·20
0·914	51·88	59·74	104·63
0·916	50·98	58·83	103·05
0·918	50·08	57·92	101·43
0·91976	49·28	57·10	100·00
0·920	49·17	56·99	99·80
0·922	48·25	56·05	98·16
0·924	47·33	55·10	96·49
0·926	46·40	54·14	94·80
0·928	45·47	53·16	93·09
0·930	44·53	52·18	91·36
0·932	43·59	51·18	89·61
0·934	42·62	50·15	87·81
0·936	41·64	49·10	85·97
0·938	40·65	48·04	84·10
0·940	39·65	46·95	82·19
0·942	38·64	45·85	80·26
0·944	37·60	44·71	78·26
0·946	36·54	43·54	76·21
0·948	35·46	42·35	74·12
0·950	34·37	41·13	71·98
0·952	33·25	39·87	69·76
0·954	32·09	38·57	67·48
0·956	30·90	37·20	65·09
0·958	29·66	35·79	62·60
0·960	28·39	34·33	60·03
0·962	27·06	32·79	57·33
0·964	25·68	31·18	54·51
0·966	24·23	29·48	51·53
0·968	22·71	27·69	48·38
0·970	21·14	25·83	45·14
0·972	19·53	23·91	41·77
0·974	17·90	21·96	38·35
0·976	16·25	19·98	34·87
0·978	14·61	18·00	31·42
0·980	12·99	16·04	27·99
0·982	11·42	14·13	24·66
0·984	9·91	12·29	21·44
0·986	8·46	10·51	18·34
0·988	7·08	8·80	15·38
0·990	5·76	7·18	12·53
0·992	4·51	5·63	9·82
0·994	3·31	4·14	7·24
0·996	2·17	2·71	4·73
0·998	1·07	1·34	2·33
1·00000	0·00	0·00	0·00

comprehensive and exact of the researches hitherto made in the field of alcoholometry. Mendeléeff obtained alcohol of a specific gravity 0·79425 at 15°/15°, which at 15·6°/15·6° is equivalent to 0·79384 in a vacuum, or to 0·79359 in air, and he assigned to Drinkwater's alcohol an alcoholic content of 99·95 p.c., and to the strong spirit of Blagden and Gilpin 89·06 p.c. by weight. The results of Tralles' and Gay-Lussac's experiments, being based on alcohol less dehydrated than that of Drinkwater, compare less favourably with those of Mendeléeff.

Mendeléeff was so well satisfied with the work of Blagden and Gilpin, and Drinkwater, that, for spirituous mixtures of low strength, he included many of their results in his tables of spirit-densities, and after a critical investigation and subsequent verification by the Kaiserliche Normal Eichungs Kommission, his results have been substantially adopted as the basis of the present system of German alcoholometry in place of the relatively less accurate data of Tralles.

The results of the work of these four authorities have been incorporated in the accompanying table of spirit-densities, which may serve for the pyknometrical determination of the true strength of spirits. In the assessment of duty and in commercial transactions, the standard of strength is termed 'proof.' Spirit of proof strength is defined as 'that which at the temperature of 51°F. (10·6°C.) weighs exactly $\frac{12}{13}$ths of an equal measure of distilled water' also at 10·6°. According to the best available data this mixture of alcohol and water has a specific gravity of 0·91976 at 15·6°/15·6°, and contains 49·28 p.c. by weight and 57·10 p.c. by volume of anhydrous alcohol. Spirits which contain a greater proportion of alcohol than is contained in proof spirit are said to be of overproof strength (o.p.), and those which contain a smaller proportion are said to be of underproof strength (u.p.). Variations of temperature are deemed not to affect the fiscal strength of spirits. Spirits which are of proof strength at 10·6° are consequently deemed to be of proof strength at other temperatures, and the same applies to spirits of any other strength, provided that no change in composition has occurred. In computing the strength of a spirit mixture reference is made to the volume of proof spirit it contains, if underproof, or will produce if overproof, at the dominant temperature, which for revenue purposes in this country is fixed at 10° (50°F.). Mendeléeff's alcohol is thus found to be 75·35 overproof, or 100 volumes at 10°, when diluted with water to proof strength, yield 175·35 volumes at that temperature.

In the annexed table specific gravities of aqueous alcoholic mixtures are correlated with percentages of alcohol by weight and by volume, and fiscal proof spirit. The specific gravities are reduced to air values and represent the ratio of the weight of a given volume of spirit to the weight of the same volume of water at 15·6° under the same atmospheric conditions; they may be converted to specific gravities in vacuum by means of the expression—

$$\frac{s + 0{\cdot}0012}{1{\cdot}0012}$$

Although it is probable that the density of a spirituous liquid can be determined more accurately by the use of a pyknometer than by other means, in practical operations where regard must be had to convenience, it is preferable to employ one of the many hydrometers or alcoholometers, the stems of which are variously graduated to show densities, percentages of alcohol by weight or by volume, or again arbitrary indications which can be interpreted by suitable tables.

Since the year 1816, Sikes' hydrometer has been the legal instrument for ascertaining the strength of spirits for revenue purposes in Great Britain and Ireland, as well as in most of the British Colonies. It is made of brass, gilded, and consists of a hollow sphere provided at one pole with a graduated rectangular stem uniform in section, and at the other with a conical spindle terminating in an oval counterpoise to give stability to the instrument when floating in a liquid, and also to serve as an attachment for various poises. The graduated portion of the stem contains ten principal divisions, which are equal in length, and marked '0' at the upper, and '10' at the lower end, and between these points the stem is again subdivided to 2 tenths of a division. When the instrument is floating at the '0' mark in spirit at a temperature of 15·6°, it indicates a strength of 66·7 overproof, or 92·50 p.c. of alcohol, whilst the '10' mark corresponds to a strength of 58 overproof, or 86·11 p.c. of alcohol (by weight). For strengths weaker than these a series of nine poises or weights are used, numbered consecutively from 10 to 90. The poises are made of hammered brass, gilded, and can be attached by means of a slot in the poise to the spindle of the hydrometer. The series of principal divisions can thus be repeated ten times, reading from '0' to '100,' which latter indication represents distilled water. Sikes' hydrometer indications refer to readings on the stem at the surface of the liquid in which it is floating, the capillary meniscus being disregarded, and are interpreted into proof-strengths by means of tables which are arranged so as to identify a sample of spirits at any temperature between −1·1° (30°F.) and +37·8° (100°F.).

The hydrometer which is used for strong spirits beyond the range of the ordinary Sikes' instrument is known as the 'A' or 'Light hydrometer,' and tables proper to this instrument are also issued. It is made of brass, gilded, and graduated on the stem similarly to Sikes' hydrometer. When floating at the '0' mark in spirit at a temperature of 15·6°, it indicates a strength of 73·5 overproof, or 98·24 p.c. of alcohol, whilst the '10' mark corresponds to 66·7 overproof, or 92·50 p.c. of alcohol by weight, the strength proper to the '0' mark on Sikes' hydrometer.

In the United States of America Tralles' tables are legalised, and, as in England, revenue is raised with reference to a mixture of alcohol and water termed 'proof.' American proof spirit is defined as containing one-half of its volume of Tralles' alcohol at 15·6°. For Excise purposes a series of alcoholometers are employed, each having a limited range, and indicating percentages of proof spirit—'0' representing water, '100' proof spirit and '200' alcohol—and readings at temperatures other than 15·6° are corrected by means of tables to what they

Indication of Sikes' hydrometer at 15·6°	Percentage of					Indications of hydrometer of			
	British proof spirit	American proof spirit at 15·°6	Alcohol by weight (Germany)	Alcohol by volume		Russia	Holland	Spain (Cartier)	Switzerland (Beck)
				at 15° (France)	at 15·6° (Tralles)				
	Overproof								
A.0.	73·5	198·2	98·2	98·9	99·1	—	25·3	43·5	42·6
A.1.	72·9	197·5	97·7	98·6	98·8	—	25	43·2	—
A.2.	72·2	196·8	97·2	98·2	98·4	—	—	—	41·8
A.3.	71·6	196·1	96·6	97·8	98·0	—	24·5	—	—
A.4.	71·0	195·3	96·1	97·5	97·7	—	—	42·2	40·9
A.5.	70·3	194·6	95·5	97·1	97·3	—	24	—	—
A.6.	69·6	193·8	94·9	96·7	96·9	—	—	—	—
A.7.	68·9	193·0	94·3	96·3	96·5	—	23·5	41·2	39·6
A.8.	68·2	192·2	93·7	95·9	96·1	—	—	—	—
A.9.	67·5	191·3	93·1	95·4	95·6	99·2	23	—	—
A.10 = 0	66·7	190·4	92·5	95·0	95·2	98·3	—	40·1	38·3
1	66·0	189·6	91·9	94·7	94·8	—	22·5	—	—
2	65·2	188·7	91·3	94·2	94·3	96·3	—	—	—
3	64·4	187·7	90·7	93·8	93·9	—	22	39·1	37·1
4	63·6	186·8	90·0	93·3	93·4	94·4	—	—	—
5	62·8	185·8	89·4	92·8	92·9	—	21·5	—	—
6	61·9	184·9	88·8	92·3	92·4	92·4	—	38·1	35·8
7	61·1	183·9	88·1	91·8	91·9	—	21	—	—
8	60·2	182·9	87·5	91·3	91·4	90·5	—	—	34·9
9	59·3	181·8	86·8	90·8	90·9	—	20·5	37·2	—
10	58·4	180·8	86·1	90·3	90·4	88·5	—	—	34·1
11	57·6	179·9	85·6	89·9	90·0	—	20	—	—
12	56·7	178·9	84·9	89·4	89·5	86·6	—	36·2	—
13	55·7	177·9	84·2	88·8	88·9	—	19·5	—	32·9
14	54·8	176·8	83·5	88·3	88·4	84·6	—	—	—
15	53·8	175·7	82·8	87·7	87·8	—	19	35·2	32
16	52·9	174·6	82·1	87·2	87·3	82·6	—	—	—
17	51·9	173·4	81·4	86·6	86·7	—	18·5	—	—
18	50·9	172·3	80·7	80·6	86·1	80·6	—	34·2	30·8
19	49·9	171·1	80·0	85·5	85·6	—	18	—	—
20	48·9	170·0	79·3	84·9	85·0	78·7	—	—	30
21	47·9	168·8	78·6	84·3	84·4	—	17·5	—	—
22	46·8	167·7	77·9	83·8	83·9	76·7	—	33	—
23	45·8	166·5	77·2	83·1	83·2	—	17·0	—	28·8
24	44·7	165·3	76·5	82·5	82·6	74·8	—	—	—
25	43·6	164·0	75·8	81·9	82·0	—	—	32	28
26	42·5	162·7	75·0	81·3	81·4	72·8	16·3	—	—
27	41·4	161·5	74·3	80·6	80·7	—	—	—	—
28	40·3	160·2	73·6	80·0	80·1	70·9	15·9	31·1	26·8
29	39·1	158·9	72·8	79·4	79·5	—	—	—	—
30	38·0	157·6	72·1	78·7	78·8	68·9	15·4	—	26
31	36·9	156·3	71·3	78·1	78·2	—	—	30·1	—
32	35·7	155·0	70·6	77·4	77·5	67	14·9	—	—
33	34·6	153·7	69·9	76·8	76·9	—	—	—	24·8
34	33·4	152·4	69·1	76·1	76·2	65	14·5	29·2	—
35	32·2	151·0	68·4	75·4	75·5	—	—	—	24
36	31·0	149·6	67·6	74·7	74·8	63·1	14	—	—
37	29·8	148·2	66·8	74·0	74·1	—	—	28·2	23·2
38	28·5	146·8	66·1	73·3	73·4	61·1	13·5	—	—
39	27·3	145·4	65·3	72·6	72·7	—	—	—	—
40	26·0	144·0	64·5	71·9	72·0	59·2	13·1	—	22
41	24·8	142·6	63·8	71·2	71·3	—	—	27	—
42	23·6	141·1	63·0	70·5	70·6	57·2	—	—	—
43	22·3	139·7	62·2	69·7	69·8	—	12·4	—	20·9
44	21·0	138·2	61·4	69·0	69·1	55·3	—	26·1	—
45	19·7	136·7	60·6	68·3	68·4	—	11·9	—	20·1
46	18·3	135·2	59·8	67·5	67·6	53·3	—	—	—
47	17·0	133·7	59·0	66·7	66·8	—	11·5	25·2	—
48	15·6	132·1	58·2	65·9	66·0	51·3	—	—	18·9
49	14·3	130·6	57·4	65·1	65·3	—	11	—	—
50	12·9	129·0	56·6	64·3	64·5	49·4	—	—	—
51	11·5	127·4	55·8	63·5	63·7	—	10·5	24	17·8
52	10·1	125·8	55·0	62·7	62·9	47·4	—	—	—

Indication of Sikes' hydrometer at 15·6°	Percentage of					Indications of hydrometer of			
	British proof spirit	American proof spirit at 15·°6	Alcohol by weight (Germany)	Alcohol by volume		Russia	Holland	Spain (Cartier)	Switzerland (Beck)
				at 150° (France)	at 15·6° (Tralles)				
	Overproof								
A.10=53	8·7	124·2	54·2	61·9	62·1	—	10·1	—	17
54	7·3	122·6	53·4	61·1	61·3	45·5	—	23·1	—
55	5·8	120·9	52·5	60·2	60·4	—	—	—	—
56	4·4	119·2	51·7	59·4	59·6	43·5	9·4	—	15·9
57	2·9	117·5	50·9	58·5	58·7	—	—	22·2	—
58	1·4	115·7	50·0	57·7	57·9	41·5	9	—	15·1
	Underproof								
59	0·2	114·0	49·2	56·8	57·0	—	—	—	—
60	1·7	112·2	48·3	55 9	56·1	39·5	—	21·3	—
61	3·3	110 5	47·5	55·0	55·2	—	8·3	—	14
62	4·8	108·7	46 6	54·1	54·3	37·6	—	—	—
63	6·4	106·9	45 8	53·2	53·4	—	7·9	—	13·3
64	8·1	105·0	44·9	52·3	52·5	35·6	—	20·1	—
65	9·7	103·1	44·0	51·3	51·5	—	—	—	—
66	11·4	101·2	43·1	50·4	50·6	33·6	7·2	—	12·2
67	13·1	99·3	42·1	49·4	49·6	—	—	—	—
68	14·9	97·2	41·1	48·4	48·6	31·6	6·8	19	—
69	16·7	95·1	40·2	47·3	47·5	—	—	—	11
70	18·6	93·0	39 2	46·3	46·5	29·7	—	—	—
71	20·5	90·8	38·2	45·2	45·4	—	6·1	18·1	—
72	22·4	88 6	37·2	44·1	44·3	27·7	—	—	9·9
73	24·4	86·4	36·2	43·0	43·2	—	5·7	—	—
74	26·4	84·2	35·2	41·9	42·1	25·7	—	—	—
75	28·5	81·8	34·1	40·7	40·9	—	—	16·9	8·8
76	30·7	79·4	33·0	39·5	39·7	23·7	5·1	—	—
77	32·9	76·9	31·9	38·3	38·5	—	—	—	8·1
78	35·3	74·3	30 7	36·9	37·1	21·8	—	16·1	—
79	37·7	71·4	29·5	35·5	35·7	—	4·4	—	—
80	40·3	68·5	28·2	34·0	34·2	19·8	—	—	7
81	42·9	65·4	26·9	32·5	32·7	—	4·0	—	—
82	45·7	62·3	25·6	31·0	31·2	17·9	—	15	—
83	48·6	58·9	24·2	29·3	29·5	—	3·6	—	6
84	51·7	55·4	22·7	27·5	27·7	15 9	—	—	—
85	54·8	51·7	21·1	25·6	25·8	—	—	14·1	—
86	58·2	47·9	19·5	23·7	23·9	13·9	3·0	—	4·9
87	61·5	44·1	18·0	21·8	22·0	—	—	—	—
88	65·0	40·2	16·4	19·9	20·1	11·9	—	13·3	—
89	68·4	36·2	14·7	18·0	18·1	—	2·3	—	3·8
90	71·9	32·2	13·1	16·0	16·1	9·9	—	—	—
91	75·2	28·4	11·5	14·1	14·2	—	1·9	12·4	3·1
92	78·4	24·7	10·0	12·3	12·4	7·9	—	—	—
93	81·4	21·3	8·6	10·6	10·7	—	1·5	—	—
94	84·4	17·9	7·2	8·9	9·0	6	—	11·6	2·1
95	87·3	14·6	5·8	7·2	7·3	—	—	—	—
96	90·0	11·4	4·6	5·6	5·7	4	0·9	—	—
97	92·6	8·4	3·4	4·1	4·2	—	—	10·8	1
98	95·1	5·6	2·2	2·7	2·8	2	—	—	—
99	97·6	2·8	1·1	1·4	1·4	—	—	—	—
100	100·0	0·0	0·0	0·0	0·0	0	0	10·1	0·1

would be in the same spirit at that temperature. In comparing American with British proof it is necessary to remember that the American gallon is smaller than the British Imperial gallon, 100 British being equivalent to 120 American gallons. Consequently, 100 British proof gallons are equal to 137 American proof gallons.

Similarly, in Holland a proof standard is recognised. Dutch proof contains 50 p.c. by volume of anhydrous alcohol at 15°. As in the United States, a series of alcoholometers are employed, differing only in regard to the range of their strength indications. The alcoholometer scale is divided into 28 principal divisions or degrees, which are equal in length, and again subdivided, each principal division representing $\frac{1}{100}$ of the volume of the instrument below the zero mark. Spirit tables based on the results of Baumhauer's investigations accompany the instruments and translate degrees on the scale into percentages of alcohol at 15° on which the revenue charge is based.

In Italy Tralles' alcoholometer is used officially. This instrument is made of glass, and at the standard temperature of 15·6° directly indicates the volume of alcohol contained in 100 volumes of spirit when measured at the same temperature. Indications at other temperatures are corrected by means of tables to true percentages by volume at 15·6°.

In Austria-Hungary an alcoholometer closely resembling Tralles', and indicating percentages of alcohol by volume at 15° is used. Its indications are uniformly higher than those of Tralles' to the extent of from one or two tenths per cent. Readings on this instrument are taken at the highest point of the capillary meniscus, which extends 1–2 mm. on the stem above the normal surface of the liquid.

Tralles' alcoholometer and tables are used commercially in Russia, but for Revenue purposes a metal hydrometer with nine poises similar in character to Sikes' hydrometer is official. On this instrument, however, Sikes' indications are reversed, so that '100' is made to represent strong spirit, and '0' distilled water. The hydrometer scale is arbitrary, and indications are interpreted into percentages by volume of Tralles' alcohol at the standard temperature of 15·6°.

Previous to the year 1887, Tralles' instrument was also used in Germany. It has now been replaced by a system of weight alcoholometry, based on Mendeléeff's data, whereby the proportion by weight of alcohol is determined. The official alcoholometers are made of glass, and graduated to show percentages of alcohol by weight at 15°—apparent percentages at other temperatures being converted into true percentages by means of tables. Duty is, however, charged on the volume of anhydrous alcohol present in a spirit when measured at 15·6°. This system is therefore analogous to the British, with the exception that the dominant temperature at which British proof-strengths are computed is 10°.

In France Gay-Lussac's original volume alcoholometer and tables have been corrected to the new values for densities of mixtures of alcohol and water determined by the 'Bureau national des poids et mesures' (1884). The density of anhydrous alcohol at 15°/15° is given as 0·79433 in vacuum, as against 0·7947 assumed by Gay-Lussac, and the difference between the graduations of the old and new official instruments reaches a maximum of 0·4 p.c. for spirits containing from 20 to 21 p.c. of alcohol by volume. Thus 20° at a temperature of 15° on the new legal centesimal alcoholometer indicates spirit containing 20 p.c. by volume of alcohol, and corresponds to 20·4° on Gay-Lussac's original instrument. The French spirit tables indicate, at temperatures extending from 0° to 30°, the percentage by volume of alcohol which a liquid contains at 15°.

Previous to the adoption of Gay-Lussac's alcoholometer and tables by the French Government, Cartier's areometer was used as the Revenue instrument. Its stem is graduated from 10 to 45 in divisions of equal length, and indicates the concentration of a spirituous liquid by arbitrary degrees, which serve as spirit-strengths for charging duty. Cartier's areometer is still used in Spain and South America.

In Switzerland, Beck's hydrometer is used for spirit assaying, and, like Cartier's instrument, of which it is a modification, floats at the lowest indication in distilled water at 12·5° (10°R.).

By means of the above table the indications of any one of these instruments at 15·6° can be converted into degrees of any other, and British fiscal strengths compared with those of other countries.

An indispensable step to a correct assay of spirit is the removal of any foreign matter which may be in solution in the alcoholic mixture. In the case of potable spirits, wines, liqueurs, &c., the spirit is freed from saccharine and other dissolved matter by distillation. The distillation of a strong spirituous liquid into its own volume so as to obtain an accurate determination of the amount of alcohol present is impracticable with the apparatus and the methods of distillation commonly used, so that although it is possible to distil without loss spirits of underproof strength into the same volume, it is necessary to dilute overproof spirits and distil into two, three, or four times the original volume. The amount by which the true alcoholic strength of brandy or rum differs from the apparent strength, as indicated by the hydrometer or a density determination, is termed the 'obscuration.'

In the case of medicinal preparations, flavouring essences, &c., which yield distillates containing essential oils and volatile substances, special treatment is necessary before a pyknometrical determination of spirit is possible. In these circumstances the sample or distillate is mixed with water in a separator so that the mixture shall contain not more than 20–25 p.c. by volume of alcohol, and common salt is added in quantity sufficient to saturate the liquid. The mixture is then shaken vigorously with 50–100 c.c. of light petroleum, and after remaining a short time, the aqueous layer is extracted, if necessary, a second time with petroleum (for instance when chloroform or ether is present), and finally drawn off into a flask and distilled. In the case of soap liniments and similar preparations, dilute sulphuric acid is used instead of salt, and the aliphatic acids and volatile matters removed by petroleum before distilling (Chem. Soc. Trans. 1903, 314). Preparations containing iodine are decolourised with sodium thiosulphate, and excess of caustic soda added to prevent decomposition of the tetrathionate during distillation. Similarly, volatile acids must be neutralised, and ammoniacal liquids distilled from dilute sulphuric acid solution.

For the estimation of ethyl alcohol in fusel oil, or liquids containing fusel oil, the salt-petroleum process may be employed, but as the higher alcohols cannot be wholly eliminated by this method, the specific refraction of the distillate is determined by the Zeiss Immersion Refractometer. The refractions of mixtures of ethyl alcohol and water have been determined at various temperatures by Wagner and Schultze (Zeitsch. anal. Chem. 1907, 508) and others, and a near approximation to the true alcoholic content of a fusel oil mixture, treated as above described, can be obtained by applying to the apparent percentage by volume of alcohol, as indicated by the density of the distillate, a subtractive correction of 0·5 p.c. for each degree of difference between the refractometer reading as found at 15·6°, and that required for a mixture of ethyl alcohol and water corresponding to the ascertained density. This method of eliminating foreign matters in spirit assaying, from a knowledge of their influence on the specific refractions of aqueous alcoholic mixtures, is capable of wide application, and has been utilised, for instance, by Leach and Lythgoe (Amer. Chem. J. 1905, 964) for determining the proportion of methylated spirits in a spirituous liquid (v. REFRACTOMETER). J. H.

ALCORNIN or **ALCORNOL.** An alcohol, $C_{22}H_{24}O$, of the nature of phytosterol, found in Alcornoco bark (Hartwich and Dünnenberger, Arch. Pharm. 1900, 341).

ALCOVINOMETER. An instrument for determining the alcoholic content of a wine by observing its ascent in a capillary tube.

ALDEHYDE, *Acetaldehyde* C_2H_4O or $CH_3{\cdot}CHO$. A product of the oxidation of ordinary (ethylic) alcohol. Aldehyde occurs, together with its polymerides metaldehyde and paraldehyde, in the 'first runnings' from the stills in the rectification of alcohol which has been filtered through charcoal (Kramer and Pinner, Ber. 2, 403; 4, 787; Johnson, J. Soc. Chem. Ind. 8, 57; Hewitt, *ibid.* 21, 97); the best yield is obtained from the alcohol manufactured from potatoes and from the sugar beet. It is also present in crude wood spirit (Krämer and Grodzki, Ber. 9, 1921); in crude petroleum (Robinson, J. Soc. Chem. Ind. 18, 232); in wine during the process of ageing (Trillat, Compt. rend. 136, 171; *idem.* Ann. Inst. Pasteur, 22, 704, 753, 876; *idem.* Bull. Soc. chim. 5, 546, 550; 7, 71); and in certain circumstances in the fermentation products of alcohol (Trillat, Compt. rend. 146, 645; Trillat and Souton, 146, 996; Kayser and Demolon, 146, 783; Trillat and Souton, Bull. Soc. chim. 7, 244; Ann. Inst. Pasteur, 24, 302; Kostychev, Zeitsch. physiol. Chem. 79, 130; 83, 93; 89, 367; 92, 402; Biochem. Zeitsch. 64, 237; Kostychev and Hübbenet, Zeitsch. physiol. Chem. 79, 359; 85, 408; Neubey and Kerb, Biochem. Zeitsch. 43, 494; 64, 251; Ber. 47, 2730; Grey, Biochem. J. 7, 359; Buchner, Langheld, and Skraup, Ber. 47, 2550; Muller-Thurgan and Osterwald, Am. Chem. Abstr. 1916, 2274, 2474). According to Battelli and Stern (Compt. rend. soc. biol. 68, 5) it is produced in animal tissues by oxidation of alcohol through the action of alcoholase. It occurs in poplar blossoms (Kostychev, Hübbenet, and Sheloumov, Zeitsch. physiol. Chem. 83, 105), and by oxidation of certain substances, such as rhamnose (Rosenthaler, Arch. Pharm. 251, 587). Kerbosch (Rec. trav. chim. 34, 235) showed the presence of traces of acetaldehyde in the latex of *Hevea braziliensis*. It is possibly also a degradation product of glucose in the animal body, and may be reduced to alcohol by the liver (*cf.* Embden and Baldes, Biochem. Zeitsch. 45, 157).

Aldehyde is also formed when calcium formate is heated with calcium acetate (Limpricht, Annalen, 97, 369), and when lactic acid and the lactates are distilled with manganese dioxide and sulphuric acid (Stadeler, Annalen, 79, 333); or by the action of dilute sulphuric acid alone on lactic acid.

$$CH_3CH(OH){\cdot}COOH = CH_3{\cdot}CHO+HCOOH$$

(Erlenmeyer, Zeitsch. f. Chemie, 1868, 343), a process used commercially at one time for the production of aldehyde for the preparation of Aldehyde Green. It is also one of the products of the dry distillation of sugar (Völckel, Annalen, 87, 303).

Preparation.—Aldehyde is formed by the oxidation of alcohol by means of platinum black (Döbereiner, Gm. 8, 274), of manganese dioxide and sulphuric acid (Liebig, Annalen, 14, 133), of potassium dichromate and sulphuric acid (Stadeler, J. 1859, 329), of metallic catalysers (Bouveault, Bull. Soc. chim. 1908, 3, 117; Sabatier and Senderens, Compt. rend. 136, 738); or when alcohol is passed through an iron tube heated to 710°–750° (Ipatieff, Ber. 34, 596).

According to Lang (J. Soc. Chem. Ind. 22, 571), the most useful oxidising agents for converting alcohol to aldehyde are the manganic salts. When prepared by Liebig's method, 2 parts of 80 p.c. alcohol are heated with 3 parts of manganese dioxide, 3 parts of sulphuric acid, and 2 parts of water, and the distillation carried on until the distillate begins to show an acid reaction; this point is reached when about three parts have collected in the well-cooled receiver. The distillate containing alcohol, acetal and ethereal salts is then distilled with an equal weight of calcium chloride, and 1½ parts collected; this is again rectified with an equal weight of calcium chloride and ¾ part distilled over. The product so obtained is nearly anhydrous, but still contains alcohol and small quantities of ethereal salts; to free it from these, it is dissolved in 2 vols. of ether, saturated with ammonia in the cold, and the aldehyde-ammonia which separates is collected, dissolved in water, distilled with dilute sulphuric acid in a water-bath, and the distillate rendered anhydrous by rectification over calcium chloride at as low a temperature as possible.

Improved methods and apparatus for oxidising alcohol into aldehyde are described by Boult, Eng. Pat. 3998, 1896; J. Soc. Chem. Ind. 15, 668; Fournier, Eng. Pat. 7887, 1897; J. Soc. Chem. Ind. 16, 695.

Ethylene oxide $(CH_2)_2O$ (the anhydride of glycol) yields acetaldehyde on heating (Nef, Annalen, 335, 201), particularly in presence of aluminium oxide at 200° C. (Ipatieff and Leontowitsch, Ber. 36, 2017).

It is also produced by treating ethylene glycol with Fenton's reagent, or by treating ethylene diamine with nitrous acid (Neuberg and Rewald, Biochem. Zeitsch. 67, 127), and from pyruvic acid by heating to 150° C. with dilute sulphuric acid (Beilstein and Wiegand, Ber. 17, 841)

$$CH_3{\cdot}CO{\cdot}COOH = CH_3{\cdot}CHO+CO_2$$

A process claimed by the Fabrique de Produits de Chimie Org. de Laire (Eng. Pat. 5533, 1913) consists in heating ethyl halide with hexamethylenetetramine or formaldehyde and ammonia.

Various aliphatic acids, such as succinic, glyceric, maleic, fumaric, tartaric, crotonic, &c., yield acetaldehyde on treatment with Fenton's reagent in sunlight (Neuberg, Biochem. Zeitsch. 67, 50). Behrens (D. R. P. 276764) describes the production of acetaldehyde by mixing the gases obtained by distilling coal, wood, turf, &c., with 5–6 p.c. of carbon dioxide and heating the mixture for some time. Snelling (U. S. Pat. 1124347) claims the production of aldehyde by passing the vapour of ethyl alcohol into a porous earthenware tube, which may be lined with platinum or palladium, heated to about 800°, and drawing off the hydrogen produced in the reaction which diffuses through the walls of the tube; the emoval of the hydrogen allows the reaction to proceed more nearly to completion.

The most convenient laboratory method is that of Sabatier and Senderens (*l.c.*), by passing alcohol vapour over metallic copper heated to about 300° C. (*cf.* also Eng. Pat. 17259, 1911). Aldehyde *is also formed to some* extent by heating charcoal, saturated with acetylene, to 350° C. with water (Degrèz, Ann. Chim. Phys. [7] 3, 216).

Commercially, aldehyde can be obtained from the 'first runnings' of the alcohol stills. A special form of still in which the separation of aldehyde from alcohol is brought about during the rectification of the latter is figured and described by Galland (Dingl. poly. J. 259, 225).

Production from Acetylene.—Within the last few years the commercial production of acetaldehyde from acetylene has become increasingly important, thereby offering new routes for the production of ethyl alcohol, acetic acid, acetone, and so on.

This process depends on the discovery of Kutscherow (Ber. 14, 1540; 17, 13), that in the presence of mercury salts, such as mercuric chloride, acting as catalysts, acetylene reacts with water to give acetaldehyde:

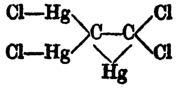
$$CH \vdots CH + H_2O = CH_3{\cdot}CHO$$

This result appears to be due to the intermediate formation of a compound

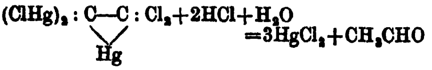
$$(ClHg)_3 \vdots C{\cdot}CHO$$

(trichlormercuriacetaldehyde), which is split up by water to form mercuric chloride and acetaldehyde (Kutscherow, *l.c.*; 42, 2759; Keiser, Amer. Chem. J. 15, 537; Biginelli, Chem. Zentr. 1898, i. 926; Hofmann, Ber. 31, 2212, 2783; 32, 874; 37, 4459; 38, 663; Hofmann and Kirmreuther, Ber. 41, 314; 42, 4232; Biltz and Mumm, Ber. 37, 4417; 38, 133; Annalen, 404, 219; Brame, Trans. Chem. Soc. 87, 427; Erdmann and Köthner, Zeitsch. anorg. Chem. 18, 48; Béhal, Ann. Chim. Phys. [6] 15, 267).

According to Hofmann (*l.c.*) the compound formed has the structure:



and is formed by the addition of two molecules of mercuric chloride to one of mercuric carbide HgC_2, which is then split up by water:



$$(ClHg)_2 : C{-}C : Cl_2 + 2HCl + H_2O = 3HgCl_2 + CH_3CHO$$

(*cf.* Soc. Anon. nouvelle l'Oyonnith, Fr. Pat. 420436). (For further details see ACETYLENE.)

The first English patent dealing with the matter is by the Chem. Fab. Griesheim Elektron (Eng. Pat. 29073, 1910), according to which aldehyde and its polymerisation products, such as paraldehyde and crotonic aldehyde, are produced by the reaction of acetylene with a solution of a mercury salt in an organic or inorganic acid at a temperature below 70° C. Such suitable acids are sulphuric, phosphoric, acetic, chloracetic, &c., the use of 45 p.c. sulphuric acid mixed with mercuric oxide is also recommended at temperatures below 70°. The Consortium f. Elektrochemische Industrie (Eng. Pat. 6000, 1913) describe a modification consisting in passing acetylene through sulphuric acid solutions of mercury oxides containing not more than 60 parts SO_4 in 1000 parts of water, and working at temperatures over 70° C. The aldehyde formed distils off, and mercury is deposited at the bottom of the liquid; the patent also describes an electrolytic process for reoxidising the mercury which is gradually deposited by reduction during the process. The same firm later (Eng. Pat. 16848, 1913) claim a process in which an excess of acetylene is passed through the catalytic solution, the aldehyde formed is carried away in the gas stream, from which it is then removed, and the acetylene passed back to the catalyst.

Bayer & Co. (Eng. Pat. 6527, 1914), (void) claim a process similar to the foregoing, but in which the sulphuric acid is replaced by an organic sulphonic acid, such as the sulphonic acids of benzene, *o*-chlorphenol, naphthalene, or the corresponding di- or tri- sulphonic acids, &c. The chief purpose of using such acids is to avoid the condensation and polymerisation of the acetaldehyde caused by prolonged action of stronger acids such as sulphuric.

Chem. Fab. Griesheim Elektron (Eng. Pat. 15669, 1914) describe the use of a 20–35 p.c. acid mixed with a mercury salt, the temperature being kept below the boiling-point of the acid; sulphuric, phosphoric, or organic sulphonic acids are specified as suitable.

G. Boiteau (Eng. Pat. 15919, 1914), in dealing with the production of a catalytic liquid, produced by dissolving a mercuric salt in a suitable solvent and then forming the sulphate *in situ* by the addition of sulphuric acid, is chiefly concerned with the production of ethylidene diacetate.

A further improvement claimed by the Consortium (Eng. Pat. 16957, 1914) consists in passing an excess of acetylene through a hot solution containing mercury compounds and so adjusting the conditions that a state of thermal equilibrium is approximately attained. This is carried out by adjusting the rate of flow of the gas and the temperature of the reaction vessel, so that the heat evolved by the reaction is balanced by the heat lost by evaporation of water and by addition of fresh water to keep the volume of liquid constant; the reaction may be carried out in thermally insulated vessels surrounded by a water jacket; a temperature of 80° is said to be suitable, using sulphuric acid of 6–35 p.c. strength.

H. W. Matheson, of the Canadian Electro-products Company, describes a process which consists in passing acetylene in excess into sulphuric acid of 6 p.c. strength containing mercuric oxide in suspension, at 40–65° C. and at pressures varying from atmospheric to 3–4 lbs. above: the process is made continuous by the periodic addition of the necessary amounts of water, acid and mercuric oxide. (Eng. Pat. 132557.)

To overcome the difficulty caused by the gradual separation of mercury as a heavy sludge, which is difficult to deal with, Meister, Lucius,

and Brüning (Eng. Pat. 24153, 1914) suggest the introduction of suitable oxidising agents to the reaction liquid, such as ferric salts, chromic acid, or chromates, to prevent the separation of metallic mercury (*cf.* U.S. Pat. 1151928, 1151929; D. R. P. 293070).

A method for overcoming this trouble is given by T. P. Hilditch and J. Crosfield and Sons consisting in the periodic addition of small amounts of suitable oxidising agents such as manganates, permanganates or hydrogen peroxide to reoxidise the sludge to mercuric oxide. (Eng. Pats. 124702, 125926.) Lead peroxide, ceric oxide and manganese dioxide are also claimed (Eng. Pat. 131086).

The Consortium (Eng. Pat. 5132, 1915) state that satisfactory results are obtained by the use of solvents, such as glacial acetic acid, mixed or not with vinyl acetate, ethylidene diacetate, &c., in the presence of mercuric oxide and strong acids; water is added in the theoretical proportions and the temperature kept at 80°–90°. The use of iron or nickel apparatus is also suggested.

The difficulty caused by the formation of the mercury sludge is also discussed by the Chem. Fab. Griesheim Elektron (Eng. Pat. 10140, 1915), who claim the recovery of the mercury by carbonising the residue by heat, or by mixing the sludge with caustic soda and electrolysing.

The Soc. Chem. Ind. in Basle regenerate the catalyst by electrolysis in presence of a suitable oxygen-carrier such as an iron salt (Eng. Pat. 130138).

H. Dreyfus (Eng. Pat. 105064), in a somewhat lengthy claim, states that the production of acetaldehyde is conveniently carried out by observing one or more of the following conditions:—

(1) Sulphuric acid is employed of 5–20 p.c. (2) Less than 20 p.c. of mercury compounds are used. (3) The temperature is kept below 60° C. (4) The acetylene is rapidly introduced in such quantity that it is all absorbed. (5) The acetylene is at first introduced slowly until all the mercury compound becomes grey or greyish-black. (6) After a quantity of aldehyde has been formed the introduction of acetylene is stopped and the temperature raised to distil off the aldehyde, after which the temperature is again lowered and more acetylene introduced. (7) The acetylene is previously purified from sulphuretted hydrogen, phosphine, ammonia, &c. (8) Water is added throughout the reaction to keep the percentage of acid constant. (9) The absorbing solution is first heated up to dissolve all the mercury compounds and then cooled to the temperature suitable for the reaction. (10) The mixture of gas and liquid is strongly agitated, and the acetylene is introduced under slight pressure; in place of sulphuric acid other acids, such as benzene sulphonic acid or phosphoric acid, may be used. The aldehyde may be removed from the solution by evacuation or by solvents such as acetylene or ethylene chlorides or benzene, instead of by distillation. The mercury residue may be regenerated by treatment with suitable oxidising agents; the process may be carried out in lead-lined apparatus, the surface of which is previously coated with a layer of lead sulphate, or iron apparatus lined with acid resisting plates or earthenware may be used. The use of suitable heating and cooling pipes is also described. The same inventor, in a patent of addition to the above (Eng. Pat. 106483), claims a modification of the principal process, using sulphuric acid of over 20 p.c. strength and extracting the aldehyde by means of a solvent such as derivatives of acetylene, ethylene, or benzene.

Dreyfus also claims the use of iron-silicon alloy vessels for the process, which are resistant to hot dilute sulphuric acid and to the action of mercury (Eng. Pat. 115899).

In Eng. Pat. 107584, the Deutsche Gold and Silber Scheide Anstalt describe a distinctly different process, consisting in passing a mixture of acetylene and steam over contact agents, such as molybdic acid on asbestos, at high temperatures; somewhat similar is the proposal of Chemische Fabrik Rhenania (Eng. Pat. 109983), to pass acetylene and steam over bog-iron ore at 400°–420°; in place of bog-iron ore, hydrated iron oxide, bauxite, hydrated aluminium silicates, or compounds of copper, nickel, cobalt, manganese, chromium, cerium, or vanadium may be used. (*Cf.* also Eng. Pat. 107585.)

Of later developments we may note that Hibbert and Morton (U.S. Pats. 1213486; 1213487; 1247270; Can. Pats. 181655; 181656; 181657) recommend the introduction into the catalytic mercury solution of a salt of a weak acid, specifically a borate; the absorption of the acetylene and the distillation of the acetaldehyde is said to be more rapid and complete, and the tendency to the formation of undesirable by-products is said to be greatly reduced. They also claim the use of several catalytic baths arranged in series so that the vapours pass through them all in succession.

The Comp. des Produits chim. d'Alais, in Eng. Pat. 130650, describe the production of acetaldehyde from acetylene in an apparatus in which the reaction liquid is subjected continuously to a vacuum so as to remove the aldehyde as formed.

As actually carried out on the large scale at the Shawinigan works of the Canadian Electro products Co., acetylene gas is led into dilute sulphuric acid containing mercuric oxide in suspension, the oxide being led in continuously and the acetaldehyde removed by the large excess of acetylene used: the requisite oxide is prepared by electrolysing mercury in large cast iron pots 6 ft. in diameter and 15 ins. high using the mercury as the anode and dilute caustic soda as the electrolyte. (Can. Chem J. III. 260 (1919).)

Substituted acetaldehydes applicable to perfumery can be obtained by condensing a ketone with a halogen or amino substituted acetic ester in the presence of sodium. The α-hydroxy acrylic ester thus obtained is saponified and decomposed by heat or distillation under reduced pressure (J. Soc. Chem. Ind. 23, 455).

Properties.—Aldehyde is a colourless liquid b.p. 20·8°, m.p. −120·7°, and sp.gr. 0·80092 at 0° (Kopp, Annalen, 64, 214); 0·79509 at 10° 0·79138 at 13°, 0·78761 at 16° (Perkin, Chem Soc. Trans. 45, 475). It has an extremely pungent suffocating odour; it is very inflammable, and burns with a feebly luminous flame.

It is soluble in all proportions in alcohol, ether, and water, and is separated from the aqueous solution as an ethereal layer on addition of calcium chloride. It possibly forms an addition compound with water

$$CH_3·CHO+H_2O = CH_3·CH(OH)_2$$

(*aldehydrol; ethylidene glycol*) (Ramsay and Young, Trans. Roy. Soc. 1886, i. 117; Perkin, Trans. Chem. Soc. 51, 815; Binot and Pickering, *ibid.* 71, 774; Homfray, *ibid.* 87, 913; Colles, *ibid.* 89, 1249). When heated with aqueous soda, potash, or barium hydroxide, so-called aldehyde resin is obtained as a brown mass (Liebig, *l.c.*; Weidenbusch, Annalen, 66, 153; Lederer, Monatsh. 22, 536). Sodium amalgam converts aldehyde into ethyl alcohol, a small quantity of β-butyleneglycol, which is also formed by the action of magnesium amalgam (Meunier, Compt. rend. 134, 473; Tistschenko and Grigoreeff, J. Russ. Phys. Chem. Soc. 38, 540; Voronkoff, *ibid.* 38, 547), being formed simultaneously (Kekulé, Annalen, 162, 310). With sodium, acetaldehyde reacts violently, producing the compound $CH_2 : CH·ONa$, which rapidly polymerises to a brown substance, whilst if the reaction takes place in presence of benzoyl chloride in ethereal solution aldehydoaldolbenzoate $C_{13}H_{16}O_4$, m.p. 86°-87°, is formed (Freer, Amer. Chem. J. 18, 552; Annalen, 293, 326). Phosphorus pentachloride reacts with it, yielding ethylidene dichloride (Geuther, Annalen, 105, 323). With potassium cyanide alanine and α-imino dipropionic acid are formed (Franzen and Ryser, J. pr. Chem. 88, 293).

Reduction of Aldehyde.—In presence of reduced nickel hydrogen reduces aldehyde to ethyl alcohol, a good yield and pure product being obtained (Sabatier and Senderens, Compt. rend. 137, 301). Modifications of this process have been worked out and patented. Thus, H. Dreyfus (Eng. Pat. 108856) describes the production of ethyl alcohol by the action of hydrogen on acetaldehyde in the presence of suitable catalysts such as platinum, platinised asbestos, copper, iron, chromium, nickel, cerium, uranium, vanadium, and their oxides, &c. The reaction is carried out by passing the mixture of hydrogen and aldehyde vapour through reaction vessels or tubes at temperatures ranging from the boiling-point of aldehyde to 400° C., and condensing the product. The Elektrizitäts Werke Lonza (Swiss Pat. 74129, 1917) claim the production of alcohol by passing aldehyde vapour and a large excess of hydrogen over a heated catalyst (Eng. Pat. 120163; *cf.* also 128929). It is understood that the last-named firm has been granted a concession from the Swiss Government to manufacture 7000 tons of alcohol a year from calcium carbide at their works at Visp in the Rhone Valley, and are to supply not less than 2500 tons alcohol to the Government J. Ind. and Eng. Chem. 1917, 903). An acetic acid factory is also being constructed at Wallis.

For the production of one ton of alcohol by this process about one ton calcium carbide is necessary, and 500 cubic metres of hydrogen; the former requires some 8000 kw. hours and the latter about 3000 kw. hours. In addition each ton alcohol requires 2500 kg. of coal and 4000 kg. limestone (Chem. Ind. 1917, 335).

Oxidation of Aldehyde.—With potassium permanganate, acetic acid is formed, but in presence of excess of potash, oxalic and carbonic acids are also formed (Denis, Amer. Chem. J. 38, 561).

It has been found possible to oxidise acetaldehyde on a commercial scale by means of oxygen or air in the presence of a suitable catalyst. The various patented processes may be divided into two classes:—

(1) Where air or oxygen is passed into the liquid aldehyde containing a dissolved catalyst.

(2) Where the two substances are passed over a heated catalyst.

(1) The Consortium f. Elektrochemische Industrie (Eng. Pat. 16849, 1913) claim the production of per-acetic acid by treating acetaldehyde with oxygen at a low temperature, preferably with the exclusion of injurious impurities, such as water and manganese compounds. The reaction is said to be facilitated by the use of chemically active rays. On allowing per-acetic acid obtained from acetaldehyde to attain the room temperature it is decomposed by the remaining aldehyde into acetic acid.

(From this it would seem possible that in the various processes next to be described, the first stage in the production of acetic acid is the addition of oxygen to form per-acetic acid $CH_3·CHO+O_2=CH_3·CHO·O_2$, which then reacts with acetaldehyde, yielding acetic acid:

$$CH_3·CHO·O_2+CH_3·CHO=2CH_3·COOH.)$$

The same patentees next described (Eng. Pat. 17016, 1913) the production of acetic acid by oxidising aldehyde by means of air or oxygen in the presence of a manganese compound acting as a catalyst. The catalyst is preferably employed in the dissolved or colloidal condition which may be prepared by introducing permanganates into the aldehyde when reduction takes place to a catalytically active brown liquid.

In Eng. Pat. 17018, 1913, the Consortium describe a modification of Eng. Pat. 16849, 1913, consisting in obtaining per-acids by adding certain metal salts, other than manganese compounds, such as compounds of chromium, cobalt, iron, uranium, and vanadium. The use of ferric acetate is claimed by Th. Dreyfus in Eng. Pat. 130035.

A further modification of Eng Pat. 17016, 1913, is claimed by the Consortium (Eng. Pat 7418, 1914), consisting in substituting for permanganates the formate, acetate, butyrate, benzoate, lactate, or other organic salt of manganese.

Meister Lucius and Brüning (Eng. Pat. 10377, 1914) assert that greatly improved results are obtained by passing in the air or oxygen under pressure; thus, for instance, oxygen at a pressure of two atmospheres is passed into acetaldehyde containing 1 p.c. by weight of ceric oxide; the temperature rises to 50°-60°, and cooling is necessary. Yields up to 95 p.c. are claimed; as catalysts are mentioned also ferric oxide, vanadium pentoxide, chromium oxide, and platinum black. A table is given, showing the influence of pressure:—

Acetic Acid obtained p.c. of Theoretical Yield.

	With catalyst.	With pressure.	With pressure and catalyst.
After 1 hour,	4 p.c.	5 p.c.	35 p.c.
After 5 hours,	16 p.c.	20 p.c.	95 p.c.

A somewhat different process is given in Eng. Pat. 14113, 1914, by the Chemische Fabrik Griesheim Elektron, consisting in manufacturing acetic acid by passing acetylene and oxygen alternately or simultaneously into acetic, chloracetic, lactic, or other organic acid containing water, to which has been added a mercury compound with or without the addition of bisulphate, sulphuric acid, &c. Aldehyde is first formed when passing in acetylene, and is then oxidised to acetic acid by the oxygen subsequently introduced. This proceeding sounds, however, somewhat dangerous, and is probably less easily controlled than the others. The B.A.S.F. claim a process for carrying out the oxidation by means of air or oxygen in presence of iron compounds and organic salts of alkalis and alkaline earths, including magnesium and aluminium (D. R. P. 294724).

(2) The second method is described by the Chem. Fab. Griesheim Elektron (Eng. Pat. 17424, 1911), and consists in adding acetic acid, chloracetic acid, or acetic anhydride to the aldehyde before the commencement of the oxidation. A catalyst such as vanadium pentoxide, uranium oxide, or roasted ferrosoferric oxide, Fe_3O_4, facilitates the reaction. The process may be conducted in tubes or towers, &c., packed with glass or clay. In an addition to this patent (8076, 1912) an improvement is claimed consisting in treating small quantities of aldehyde with oxygen in vessels, tubes, towers, &c., until the greater part is oxidised to acetic acid, and then adding further quantities of aldehyde and passing a stronger current of oxygen, whereby oxidation proceeds rapidly. The process may be accelerated by the addition of a catalyst, such as those already mentioned.

H. Dreyfus (Eng. Pat. 105065) claims the production of acetic acid by passing a mixture of aldehyde vapour with air or oxygen through vessels or tubes containing contact substances, such as platinised asbestos, preferably at a temperature above the boiling-point of acetic acid; the mixture of aldehyde vapour and air or oxygen may be preheated to a suitable temperature before entering the contact apparatus; the heat of the gases issuing from the contact apparatus may be utilised for this purpose, the process being carried out in apparatus similar to that employed in the manufacture of sulphuric anhydride by the contact process.

The same inventor in a later patent (Eng. Pat. 108459) describes a further modification of the previous process consisting in oxidising acetaldehyde by means of air or oxygen at temperatures of 150°-250° C. either in presence or absence of a catalyst. Suitable catalysts are stated to be: platinum, copper, copper oxide, chromium oxide, uranium oxide, vanadium oxide, cerium oxide, iron, pumice, &c. The gases are preferably caused to travel through a long path in the reaction apparatus, and the air employed is preferably in excess of the theoretical amount. Further improvements given in Eng. Pat. 110545, by the same patentee, are chiefly concerned with minor details; thus the mixture of aldehyde vapour and air may be obtained by passing air through liquid aldehyde and passing the mixture into the reaction chamber; or liquid aldehyde may be vaporised by a current of air in the bottom of the reaction chamber itself, the latter being provided with suitable agitators. The temperature of the liquid aldehyde or of the air may be regulated so as to control the composition of the mixture of vapour and gas, or the liquid aldehyde may be suitably diluted, say, with acetic acid for the same purpose. The liquid acetic acid formed collects in a suitable part of the apparatus and flows away, while the issuing gas containing aldehyde may be treated again, or the contained aldehyde may be recovered and re-used (*cf.* Fr. Pat. 479656, and additions 20201, 20202).

In Eng. Pat. 116279, S. Utheim claims the production of acetic acid from aldehyde by the action of oxygen under pressure, the aldehyde being supplied to the oxygen in a confined space in limited quantities, *e.g.* in a number of narrow tubes with suitable cooling. Whilst the Comp. des Prod. chim. d'Alais describe the oxidation as taking place in suitable towers by means of air or oxygen in absence of a catalyst, the product being heated continuously to destroy any peracetic acid formed (Eng. Pat. 130651).

The process described in Eng. Pat. 109983 by the Chemische Fabrik Rhenania falls into a somewhat different category, as it deals with the direct production of acetic acid from acetylene by passing the latter, mixed with steam, over partially reduced bog iron-ore; the process does not, however, appear to be of much importance owing to the poor yield.

Hibbert (U.S. Pat. 1230899; Can. Pat. 178237) recommends the use of wood charcoal previously saturated with strong acetic acid to promote the reaction between acetaldehyde and oxygen, using it as a packing for towers through which the mixture is passed. A 90 p.c. yield of 70 p.c. acid is obtained, working at 45° C.

W. H. Matheson, of the Canadian Electro-products Co., Shawinigan Fall, Quebec, states that the oxidation process carried out at these works is done in aluminium vessels, as copper, iron, etc, are unsuitable and have led to violent explosions (Can. Chem. Jour. III. 260 (1919). These works manufactured synthetic acetone and acetic acid for the British Government during the war, and from Nov., 1917, to Nov., 1919, about 10,000 tons glacial acetic acid were shipped to England, chiefly for the manufacture of acetylcellulose for aeroplane dope; at the time of the Armistice (Nov. 11, 1919), the plant had been enlarged to produce about 1600 tons per month at a total capital cost of about £800,000. According to A. F. Cadenhead (Can. Chem. Jour. III., 268 (1919)), one ton of carbide produces on an average about half a ton of acetic acid.

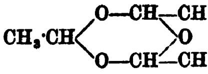
When subjected to electrolysis in faintly alkaline or neutral solution it is decomposed into alcohol and acetic acids (Slaboszewicz, Chem. Zentr. 1903, i. 279; Law, Chem. Soc. Trans. 1905, 198; Jackson and Laurie, *ibid.* 1906, 156), whilst when heated alone to high temperatures carbon monoxide and methane are the chief products (Bone and Smith, Chem. Soc. Trans. 1905, 910; Ipatieff, Chem. Zentr. 1906, i. 87; Nef, Ann. 318, 198). Action of silent electric discharge (*cf.* Besson and Fournier, Compt. rend. 150, 1238). Action of ultra-violet rays (Berthelot and Gaudechon, Compt. rend. 56, 233).

Acetaldehyde and its dimethyl derivative have antiseptic properties (Coblenz, J. Soc. Chem. Ind. 17, 728; Pasqualis, Chem. Zentr. 897, ii. 10, 12). It is also useful in photographic developing (Seyewetz, Bull. Soc. chim. 9, (3) 134), and the vapour or solution in alcohol or benzene slowly hardens dry gelatine films (Beckmann, Chem. Zentr. 1896, ii. 930; D. R. P. 116446; 116800).

Production of synthetic rubber indirectly rom aldehyde, *see* Dubosc (Caoutchouc et Gutta Percha, 9, 6608, 6713). In presence of alumina at 400° isopropyl alcohol condenses with aldehyde to give a good yield of piperylene Ostromisslensky, J. Russ. Phys. Chem. Soc. 47, 1507). By passing aldehyde and alcohol vapours over heated catalysts, such as alumina, phosphoric acid, &c., butadiene is formed Ostromisslensky, J. Russ. Phys. Chem Soc. 7, 1494, 1509). Precipitated alumina is pecially noted as, heated to 369°–460°, a 6–18 p.c. yield of pure erythrene is obtained.

Aldehyde readily polymerises in the presence of small quantities of various substances, such as sulphuric acid, phosgene, zinc chloride, hydrogen chloride, sulphur dioxide, the halogens, particularly iodine, &c., and two compounds are obtained the relative quantities of which depend upon the temperature; the chief pro-uct being *metaldehyde* $(C_2H_4O)_3$ (Hanriot and Oeconomides, Ann. Chem. Phys. [5] 25, 227; McIntosh, Chem. Soc. Trans. 1905, 790; Vecchini, Gazz. chim. ital. 22, ii. 586), when he action takes place in a freezing mixture; nd the isomeric *paraldehyde* (elaldehyde) when t occurs at the ordinary temperature.

Paraldehyde $(C_2H_4O)_3$ is prepared from cetaldehyde by the addition of a drop of con-entrated sulphuric acid, the liquid boiling up t once with almost explosive violence; the product can be purified either by freezing out below 0° and removing the liquid portion, or y washing with a little dilute sodium carbonate solution, drying over calcium chloride and rectifying (Fehling, Annalen, 27, 319; Werden-usch, *ibid.* 66, 155; Geuther and Cartmell, *ibid.* 112, 17; Geuther, Zeitsch. f. Chemie, 865, 32; Lieben, Annalen, Suppl. 1, 114 861–2; Kekulé & Zincke, Annalen, 162, 143; Brühl, *ibid.* 203, 26, 43; Franchimont, Rec. rav. chim. 1, 239; Desgrez, Bull. Soc. chim. 1, [3], 362; Wachhausen, Chem. Zentr. 1897, 493; Ciamician and Silber, Ber. 35, 1080). Polymerisation is also caused by halogen ydracids (MacIntosh, J. Amer. Chem. Soc. 3, 588). In the latter case addition products re formed, *e.g.* $(C_2H_4O)_3\cdot 3HCl$, m.p. −18°; $(C_2H_4O)_3\cdot 3HBr$, m.p. −15°; $(C_2H_4O)_3\cdot 3HI$, quid below −32°. Paraldehyde is a clear mobile colourless liquid of pleasant odour and harp taste, b.p. 124°, D_{20} 0·994, m.p. 12·5°. t possesses the same molecular weight also in he vapour phase, and in solution (Patern and asini, Ber. 19, 2529; Carrara and Terrari, azz. chim. ital. 36, i. 426). It is sparingly 12 parts paraldehyde, the solubility diminishing on warming; it does not show the characteristic aldehyde reaction; thus it does not reduce ammoniacal silver nitrate, does not resinify on heating with aqueous potash, and does not unite with ammonia or bisulphites; its formula is therefore assumed to be:



On warming with a little sulphuric acid it is readily depolymerised completely into ordinary aldehyde; many other reagents also produce the same effect; it may also occur on very long standing (Troeger, Ber. 25, 3317). Owing to the ease of depolymerisation paraldehyde is frequently made use of in place of aldehyde for many reactions where the monomolecular form is inconvenient to use owing to its low boiling-point.

Thus it condenses with diacetoneamine to form vinyldiacetoneamine (E. Fischer, Ber. 17, 1793; C. Harries, Ber. 29, 522); with aniline to form quinaldine (D. R. P. 24317; 28217; 35133; Eng. Pat. 956, 1883; 4207, 1883), and with hydroxyquinol to form yellow dyes (Liebermann and Lendenbaum, Ber. 37, 1171, 2728).

Paraldehyde sets free iodine from alkali iodides (Wachhausen, Chem. Zentr. 1897, i. 493). It is not attacked by pure nitric acid, but is readily oxidised if nitrous acid be present (Behrens and Schmitz, Annalen, 277, 313, 335).

Smits and de Leeuw assume the existence of an equilibrium of a pseudo-ternary system of aldehyde-metaldehyde-paraldehyde, the values for the different components varying according to the catalyst (Smits and de Leeuw, K. Akad. Wetenschapen, 1910, 318; Amer. Chem. Abstr. 1911, 1862; Zeitsch. physiol. Chem. 77, 268). Paraldehyde is used to some extent as a soporific.

Metaldehyde crystallises in needles or tetragonal prisms, sublimes without previous fusion at 112°–115°, and when heated in sealed tubes at 120° is entirely reconverted into ordinary aldehyde (Friedel, Bull. Soc. chim. 9, (3) 384). According to Troeger (Ber. 25, 3316), after standing for ten years a sample was converted into aldehyde and paraldehyde, but according to Hantzsch and Oechslin (Ber. 40, 4341), metacetaldehyde is not isomeric with paracetaldehyde, and is quite stable when pure. Orndorff and White (Amer. Chem. J. 16, 43) state that when it is allowed to stand for some time the metaldehyde is converted into tetraldehyde $(C_2H_4O)_4$.

Neither polymeride is resinised by aqueous soda or potash, but in other reactions they behave generally as ordinary aldehyde and yield similar products (Kekulé and Zincke).

Formation of Acetic Ester.—Another important change of the nature of polymerisation takes place under certain conditions, causing the formation of acetic ester in excellent yield.

Tischtschenko (J. Russ. Phys. Chem. Soc. 38, 398–418; Chem. Zentr. 1906, ii. 1309, 1552) proposes the following method of working: Acetaldehyde is cooled down to −20° C., uncrushed aluminium ethylate is added, and the mixture allowed to stand for several days decided that the yield of acetic ester increases with the amount of alcoholate added but only to a certain maximum limit namely 69·1 p.c. of ester (using 15 p.c. of aluminium ethylate), and that it is necessary to use the alcoholate in lumps; he also concluded that by using small quantities of the catalyst the yield of ester is lessened, with increased formation of by-products, and when only about 4 p.c. alcoholate is used the formation of by-products predominates over the ester condensation.

The Consortium f. Elektrochemische Industrie found later (Eng. Pat. 26825, 1913) that the various drawbacks could be overcome by adding to the aluminium alcoholate certain catalytic substances, such as tin chlor-ethylate, which are without catalytic activity themselves but increase the power of the alcoholate very greatly; thus, in an example, 150 parts anhydrous aldehyde were cooled down to 0° C., and 9 parts of aluminium ethylate previously fused with 10 p.c. of tin chlorethylate (from 20 parts tin tetrachloride and 14 parts absolute alcohol) were added during half an hour, with vigorous stirring and efficient cooling. After ten hours the odour of aldehyde had disappeared and the product was distilled, 96 p.c. of almost pure acetic ester coming over between 74° C. and 80° C. A comparative experiment in which the stannic chlorethylate was omitted gave only a 19 p.c. yield. In Eng. Pat. 26826, 1913, by the same firm, a further improvement is claimed, using instead of anhydrous aluminium ethylate, the same body treated with a small quantity of water or with substances containing water, in particular aluminium hydroxide. In an example the following figures are given:—

Kind of alcoholate.	Al. content.	Yield of ester.
Untreated	17·7 p.c.	21 p.c.
Fused with a little water	21·0 p.c.	87 p.c.
Untreated	17·7 p.c.	23 p.c.
Fused with $Al(OH)_3$.	24·8 p.c.	85 p.c.

The further improvements claimed in Eng. Pat. 4887, 1915 (*idem.*) consist in increasing the activity of the catalyst by dissolving in the melted alcoholate suitable substances such as dehydrated potash alum, dehydrated copper sulphate or camphor, or by supercooling the alcoholate, *e.g.* by melting and cooling rapidly by pouring into a solvent or on to a metal plate. Ethyl acetate is of special use as a solvent; the mixture of melted alcoholate and added substances mentioned above may also be dissolved in ethyl acetate; the solutions may be employed hot, or may be allowed to cool with partial separation of the alcoholate from solution.

Meister, Lucius and Brüning describe (Eng. Pat. 1288, 1915) the production of acetic ester from aldehyde by means of aluminium alcoholate, the latter being dissolved in a suitable organic solvent such as dry solvent naphtha.

(*Aluminium Alcoholate.*—The production of this catalyst is described by Farbw. v. Meister, Lucius, and Brüning in D. R. P. 286596, and addition 293613, and in 289157. According to those specifications aluminium ethoxide is obtained in good yield from aluminium and anhydrous alcohol if, in presence or absence of halogen alkyls or iodine, small amounts of mercuric chloride are added as a catalyst; other alcohols may be substituted for ethyl alcohol, yielding the corresponding alcoholates.

Upon subsequent vacuum distillation for the purpose of purifying the crude product, the aluminium ethylate goes over readily without bumping, solidifying to a snow-white mass, while mercury is not carried over with it. Or the ethylate may be distilled under atmospheric pressure without decomposition if the vapours are rapidly withdrawn from further super-heating. This may be effected by employing a low form of distilling vessel whereby condensation in the upper part of the vessel is prevented.)

Reactions.—Aldehyde in aqueous solution very readily reduces an ammoniacal solution of silver nitrate giving a bright metallic mirror. Acetaldehyde (and all aldehydes which are stable in aqueous soda solution) can be detected by adding to a solution of the suspected substance in dilute alkali a fresh solution of 1 part of paradiazobenzenesulphonic acid in 60 parts of water rendered alkaline with a little soda, and then some sodium amalgam; if an aldehyde is present, a reddish-brown colour is developed after the mixture has stood for 10-20 minutes (Penzoldt and Fischer, Ber. 16, 657).

A solution of rosaniline decolourised by sulphurous acid (Villiers and Fovolle, Compt. rend. 119, 75), or magenta bleached by sunlight (Blaser, Chem. Zentr. 1899, ii. 848), regains its original colour on addition of an aldehyde (Denigès, Compt. rend. 150, 529). This reaction is due to the formation of coloured compounds by the condensation of the aldehyde and magenta (Urbain, Bull. Soc. chim. 1896, iii. 15, 455). With salts of *m*-diamines aldehydes give coloured solutions with intense greenish fluorescence (Bitto, Frdl. 36, 369). With sodium nitroprusside and alkali, acetaldehyde gives a cherry-red colouration, whilst if tri-methylamine is first added a blue colour is produced (Bittoi Annalen, 267, 372; 269, 377; Denigès, Bull. Soc. chim. 17, (3) 381; Simon, Compt. rend. 125, 1105; Bull. Soc. chim. 19, (3) 297). Thiosemicarbazide mixed with an aldehyde in acetic, alcoholic, or aqueous solution yields characteristic thiosemicarbazones. Acetaldehydethiosemicarbazone has m.p. 146° (Freund and Schander, Ber. 35, 2602). Phenylhydrazone α-form, m.p. 98°-101°; β-form, m.p. 57° (Lockemann and Liesche, Annalen. 342, 14; Laws and Sidgwick, Trans. Chem. Soc. 99, 2085). Toschi and Angiolani (Gazz. chim. ital. 45, i. 205) recommend the use of 4-4′-diphenylsemicarbazide, the acetaldehyde derivative having m.p. 133°-134°.

Other tests for aldehydes are described by Ihl, Chem. Zeit. 14, 1571; Doebner, Ber. 27, 352, 2020; Lumière and Seyewetz, Bull. Soc. chim. 19, (3) 134; Rimini, Atti Real. Acad. Lincei, 1901, 10, 355; Murco, Compt. rend. 31, 943; Riegler Frdl. 42, 168; Behrens, Chem. Zeit. 26, 1125; Sadtler, J. Soc. Chem. Ind. 23, 387; Prud'homme, Bl. Soc. Ind. Mulhouse, 1904, 74, 169; Leys, J. Pharm. Chim. 1905, 22, 107; Auld and Hantzsch, Ber. 38, 2677.

Quantitative Estimation.—*Cf.* Rieter, Chem. Zentr. 1896, ii. 368; Rocques, Compt. rend. 127, 526, 764; Seyewetz and Bardin, Bull. Soc. chim. [3] 33, 1000; Colles, Trans. Chem. Soc. 89, 1249. Colorimetric estimation, Paul, Zeitsch. f. anal. Chem. 35, 649; Tolman, J. Amer. Chem. Soc. 28, 1624; by means of pyrrole, Sobolev and Saleski, Zeitsch. physiol. Chem. 69, 441. Estimation in presence of paraldehyde, Richter, Pharm. Zeit. 57, 125; Heyl, *ibid.* 28, 165, 720. In presence of acetone, Hagglund, Zeitsch. anal. Chem. 53, 433.

Condensation Products.—Aldehyde readily yields condensation compounds; thus when allowed to remain in the cold with dilute hydrochloric acid, or with aqueous solutions of zinc chloride or of salts having an alkaline reaction, such as potassium carbonate, aldol is obtained.

The Dupont de Nemours Powder Co. describe (Eng. Pat. 17259, 1911) the production of acetaldol by means of a solution of alkali or alkaline carbonate, borate, phosphate, or cyanide; the acetaldol so produced may be extracted with ether; or the solution may be reduced by aluminium amalgam to yield butylene glycol. A further patent by the same firm (Eng. Pat. 22621, 1912) claims the production of aldol by treating aldehyde with an alkaline substance, such as an alkali hydroxide or salt, sodium ethylate &c., dissolved in a solvent containing little or no water. Ethyl alcohol is mentioned as a suitable solvent (*cf.* also Swiss Pat. 64932; U.S. Pat. 1151113).

The Consortium f. Eletrochemische Industrie in Eng. Pat. 19463, 1913, claim the production of aldol by treating aldehyde in the absence of water with a small quantity of an alkali or alkaline earth metal, or alloy or amalgam thereof, or with their compounds with aldehyde or with other compounds of these metals that are soluble in aldehyde, such as the alcoholates or cyanides. By slow distillation *in vacuo* aldol is obtained, and by slow distillation at ordinary pressure crotonic aldehyde is formed. Organo-metallic compounds are formed by adding alkali and alkaline-earth metals to aldehyde in the absence of water (*cf.* also D. R. P. 269996).

According to N. Grünstein (Eng. Pat. 101636) aldol and other condensation products are obtained from acetaldehyde by treating the latter with quicklime or strontia; the reaction is facilitated by the addition of a trace of water. The condensation can also be effected by means of other condensing agents, such as alkaline earth metals or their carbides, such as calcium carbide, mixed or not with the oxides; the aldehyde is preferably introduced during the process. The aldol produced can be distilled *in vacuo.* Hibbert describes the production of aldol by dissolving aldehyde in gasoline and treating the solution, after cooling to −10°, with potash or caustic soda (U.S. Pat. 1086048).

Crotonaldehyde is formed when it is heated with concentrated hydrochloric acid (Kekulé, Annalen, 162, 92; Kling and Roy, Compt. rend. 144, 1111; Zeisel and v. Bitto, Monatsh. 29, 591), or with concentrated sulphuric acid (Delépine, Compt. rend. 133, 876; 147, 1316; Bull. Soc. chim. 27 [3] 7).

Aldehyde has also been condensed with other aldehydes and ketones (Wallach, Chem. Zentr. 899, ii. 1024; Schmalzhoffer, Monatsh. 211, 671; Wogrinz, *ibid.* 22, 1; Weiss, *ibid.* 25, 1065; Schachner, *ibid.* 26, 65; Salkind, J. Russ. Phys. Chem. Soc. 37, 484; Rainer, Monatsh. 25, 1035; Ehrenfreund, *ibid.* 26, 1003); with amines (Eibner and Peltzer, Ber. 33, 3460; Eibner, Annalen, 328, 121; Knoevenagel, Ber. 37, 4461); with rhodanic and substituted rhodanic acids forming stable dyeing compounds (Andreasch and Zipser, Monatsh. 24, 499; 26, 1191; Zipser, *ibid.* 23, 592; Stachetz, *ibid.* 26, 1209; Bergellini, Atti Real. Acad. Lincei, 15, 35, 181; Andreasch, Monatsh. 27, 1211; 29, 399; Wagner, *ibid.* 27, 1233); with methyl ketole forming leuco- bases of the dyes of rosaniline type (Freund and Lebach, Ber. 36, 308; Freund, Ber. 37, 322); with indole dyes, also forming leuco- bases (Loew, Ber. 36, 4326); with cyanides and cyanacetic esters (Claisen, Ber. 25, 3164; Barbier and Bouveault, Compt. rend. 120, 1269; Kohn, Monatsh. 19, 519; Wade, Chem. Soc. Proc. 1900, 156; Bertini, Gazz. chim. ital. 31, i. 265; Fiquet, Bull. Soc. chim. 7, (3) 767); with phenyl hydrazones (Fischer, Ber. 29, 793; 30, 1240; Pechman, Ber. 31, 2123; Bamberger and Pemsel, Ber. 36, 85; Lockmann and Liesche, Annalen, 342, 14; Medvedeff, Ber. 38, 16646, 2283; Maurenbrecher, Ber. 39, 3583; Laws and Sidgwick, Trans. Chem. Soc. 99, 2085); with *o*-hydroxy nitroso compounds pyrazine derivatives are formed (Lange, Ber. 42, 574). Substances capable of use in perfumery can be obtained by condensing aldehydes with negatively mono- substituted acetic acids in presence of ammonia or a primary or secondary amine (J. Soc. Chem. Ind. 24, 689, 1323). (For compounds of other substances with aldehydes, *see* Hooker and Carnell, Chem. Soc. Proc. 1893, Fischer, Ber. 27, 165; Claisen, Annalen, 237, 261; Conneler, Chem. Zeit. 20, 585; Kietreiber, Monatsh. 19, 735; Bamberger and Müller, Ber. 27, 147; Rassow, J. pr. Chem. 172, 136, 129; Betti, Gazz. chim. ital. 30, ii. 310; 33, i. 27; Koenigs, Ber. 34, 4336; Moureu and Desmots, Compt. rend. 134, 355; Knoevenagel, Ber. 36, 2136; Hann and Lapworth, Chem. Soc. Trans. 1904, 46; Simon and Conduché, Compt. rend. 138, 977; Darzens, Compt. rend. 142, 214; Eissler and Pollock, Monatsh. 27, 1129; Rolla, Gazz. chim. ital. 37, 623; Senier and Austin, Chem. Soc. Trans. 1907, 1233; Wohl, Ber. 40, 4679; Braun, Ber. 41, 2169; Zeisel and Bitto, Monatsh. 29, 591.)

Additive compounds.—Aldehyde not only shows a strong tendency to yield polymerides and condensation compounds, but unites directly with a large number of substances.

(1) Compounds with alcohols (*v.* ACETALS).

(2) Compounds with acids:—Geuther, Annalen, 106, 249; Lieben, *ibid.* 106, 336; 178, 43; Rübencamp, *ibid.* 225, 279; Schiff, Ber. 9, 304; Ponzio, J. pr. Chem. 161, 431; Schroeter, Ber. 31, 2189; Annalen, 303, 114; Delépine, Compt. rend. 133, 876; McIntosh, Amer. Chem. J. 28, 588; Wegscheider and Späth, Chem. Zentr. 1910, i. 1421 (*v.* ACETALS).

(3) Compounds with alkaline sulphites:—Aldehyde forms definite crystalline compounds when dissolved in concentrated aqueous solutions of the acid sulphites (bisulphites) of the alkali metals. The *potassium* salt $C_2H_4O,KHSO_3$ crystallises in indistinct needles; the *sodium* salt $C_2H_4O,NaHSO_3+\frac{1}{2}H_2O$, in fine needles or nacreous plates. The *ammonium* compound has the formula $C_2H_4(OH)SO_2{\cdot}NH_2$. These salts are almost insoluble in excess of the sulphite, and separate in the crystalline state; from them aldehyde can be obtained by distillation with a

stronger acid, an alkaline carbonate, or by alkali nitrites (Bunte, Annalen, 170, 305; Freundler and Bunel, Compt. rend. 132, 1338; Seyewetz and Burdin, Compt. rend. 141, 259; Rosenheim, Ber. 38, 2005; Coppock, Chem. News, 1907, 225). With hyposulphites in neutral or acid solutions aldehyde hyposulphites are obtained; $2RCHO,M_2S_2O_4$ (J. Soc. Chem. Ind. 25, 475); by varying the condition sulphoxylates of type $RCH_2{\cdot}SO_3M$ can be formed (D. R. P. 180529). Crystalline thioaldehydes are obtained by the action of hydrogen sulphide on an acidified alcoholic solution of aldehyde (Baumann and Fromm, Ber. 22, 2600; Ber. 24, 1419, 1457; Klinger, Ber. 32, 2194; Drugman and Stockings, Chem. Soc. Proc. 1904, 116; Vanino, J. pr. Chem. 185, 367).

(4) Compound with ammonia:—*Aldehyde-ammonia* $C_2H_4O{\cdot}NH_3$, obtained by leading dry ammonia into aldehyde in ethereal solution (Liebig, Annalen, 14, 144; Jean, Bull. Soc. chim. 13, (3) 474; Trillat, *ibid.* 13, (3) 689; Delépine, Compt. rend. 125, 951; 128, 105; 137, 984; 144, 853; Coninck, Compt. rend. 126, 1042; Tschitschibabin, J. Russ. Phys. Chem. Soc. 37, 1229; Duden, Bock and Reid, Ber. 38, 2036; Ciamician and Silber, Ber. 38, 1671; 39, 3942), crystallises in large rhombohedra, melts at 70°–80°, boils at 100° without decomposition, and is decomposed into its constituents on distillation with dilute acids. When hydrogen sulphide is passed through a mixture of aldehyde ammonia and ether a crystalline substance $SH{\cdot}CHMe{\cdot}NH{\cdot}CHMeOH$, m.p. 60°–63°, is obtained (Chabrié, C. R. Soc. Biol. 1896, 3, 72).

(5) Compounds with hydrocyanic acid:—(Tiemann, Ber. 14, 1965; Strecker, Annalen, 91, 349; Erlenmeyer and Passavant, *ibid.* 200, 120).

(6) Compounds with metallic salts:—With mercuric sulphate it forms the compound $SO_4:(HgO)_2:HgC_2H_4O$ (Denigès, Compt. rend. 128, 429); with mercuric nitrate, $C_2Hg_2NO_4H$ (Hofmann, Ber. 31, 2212); and with mercuric acetate alkaline solution at 0°, $CMe{\cdot}HO{\cdot}HgO$ (Lasserre, J. Pharm. 1905, 22, 246). With gold chloride it forms a coloured colloidal solution (Garbowski, Ber. 36, 1215); and with magnesium bromide, the compound $MgBr_2,3CH_3CHO$ (Menschutkin, Zeitsch. anorg. Chem. 53, 26); with calcium cyanide it forms $C_6H_{10}O_6N_2Ca_3$ (Franzen and Ryser, J. pr. Chem. 88, 293); compound with KCN (*cf.* Eng. Pat. 19463, 1913).

Substitution Products.—The action of chlorine on aldehyde has been studied by Wurtz (Annalen, 102, 93), Wurtz and Voigt (Bull. Soc. chim. 17, 402), and by Pinner (Annalen, 179, 21; Coblenz, *l.c.*; Freundler, Bull. Soc. chim. 1, (4) 66; Freundler, Compt. rend. 143, 682). Pinner finds that when chlorine is passed into ordinary aldehyde at 10°, metaldehyde and paraldehyde are first formed, and these subsequently yield substitution-derivatives, of which chloral is the chief product, butyric chloral and dichloraldehyde being formed in smaller quantity. The following derivatives have been prepared:—*Chloraldehyde* $CH_2Cl{\cdot}CHO+\frac{1}{2}H_2O$ (Natterer, Monatsh. 3, 446); with potassium cyanide and ammonium chloride, *β*-chloro-*a*-hydroxy propionic acid is formed (Raske, Ber. 45, 725); *dichloraldehyde*, $CHCl_2{\cdot}CHO$ (Grimaux and Adams, Bull. Soc. chim. 34, 29 Wohl and Roth, Ber. 40, 212); *trichloraldehyde* (*v.* Chloral).

According to S. Utheim chloroform is readily formed by acting upon aldehyde with bleaching powder in the presence of water (Eng. Pat. 116094).

The bromine derivatives, and the action of bromine on aldehyde, have been examined by Pinner (Ber. 7, 1499, and *l.c.*; Bugarsky, Zeitsch. physikal. Chem. 48, 63; Freundler, Compt. rend. 140, 1693; Mauguin, Compt. rend. 147, 747). Reactions of dibromoacetaldehyde (*cf.* Mylo, Ber. 45, 645).

Aldehyde blue is obtained by treating pararosaniline with aldehyde or, better, paraldehyde in aqueous acid solution, and precipitating the dye with sodium chloride. It is soluble in alcohol and ether, and when treated with strong hydrochloric acid is converted into a reddish yellow base which shows all the properties of a rosaniline dye (Gattermann and Wichmann, Ber. 22, 227). By slightly varying the conditions in the preparation of aldehyde blue, *aldehyde green* can also be obtained (Miller and Plöchl, Ber. 24, 1700).

F. A. M.

ALDEHYDE GREEN *v.* Triphenylmethane colouring matters.

ALDEHYDINE *v.* Bone oil.

ALDEHYDINES. Compounds formed by the condensation of ortho-diamines with aldehydes (Ladenburg, Ber. 10, 1126) (*v.* Amines).

ALDER BARK. (*Aune*, Fr.; *Erle*, Ger.) *Alnus glutinosa* (Gaert.). Used for tanning and dyeing. The percentage of tannin varies from 16 to 18 (Eitner, Zeit. f. d. Chem. Grossgew. 3, 668; 4, 279).

The tannin appears to be a methyl tannin like that of the oak; it gives a reddish-blue precipitate with ferrous acetate, an olive-green precipitate with ferrous sulphate, and is precipitated by a gum solution.

A solution of the bark is employed for obtaining black, greys, and browns on linen; in Germany for reds; and in Kamchatka for colouring skins a red tint.

ALDOFORM. A formaldehyde preparation.

ALDOL (*β-hydroxybutyric aldehyde; butanol-3-al*) $CH_3CHOH{\cdot}CH_2{\cdot}CHO$ was first obtained by Wurtz in 1872. It is produced by the action of cold dilute hydrochloric acid or other condensing agents, such as alkali acetates, carbonates or bicarbonates, or zinc chloride in aqueous solution, on acetaldehyde.

200 grams acetaldehyde at 0° C. are dropped into 200 grams water at 0° C. and 10 grams potassium carbonate are gradually added. The mixture is allowed to stand for 12–18 hours at 10° C., then shaken, first with an equal volume of ether, and again with half its volume of ether. The aqueous solution is exactly neutralised with hydrochloric acid and again extracted with half its volume of ether. The ether extracts are then united, the ether distilled off, and the residue distilled *in vacuo.* (*Cf.* art. Aldehyde.)

Aldol is a colourless liquid which boils at 83° (20 mm.), and has a specific gravity of 1·121 at 0°. It is miscible with water and alcohol. When distilled under atmospheric pressure it loses water and passes into *crotonaldehyde* $CH_3{\cdot}CH:CH{\cdot}CHO$; a similar result being obtained by heating it to 100° C. with water containing a small amount of sodium hydroxide.

As an aldehyde, it reduces an ammoniacal solution of silver nitrate.

On standing for some time aldol becomes viscous, and after some days solidifies, passing into the solid polymeric form known as *paraldol.* This form melts at 82°C., and on reduction with aluminium amalgam yields β-butylene glycol $CH_3·CHOH·CH_2·CH_2OH$.

The above compound furnishes an example of the so-called 'aldol condensation,' which has been studied at length by von Lieben and his pupils (Monatsh. 1901, 22, 289), and the requisite condition for such a reaction is that the carbon atom adjacent to the carbonyl group of the aldehyde should be united to at least one hydrogen atom, although this need not be the case when the condensation occurs between two different aldehydes, *e.g.*

$$(CH_3)_3C·CHO+R_2CH·CHO$$
$$=(CH_3)_3C·CHOH·C(R_2)CHO$$

A similar type of reaction is also possible between aldehydes and ketones, which fulfil the suitable conditions.

As a class, the aldols are colourless liquids which readily polymerise on standing. These polymerides show the same chemical reactions as the liquid forms, and are partially reconverted into such forms on distillation *in vacuo.* When distilled under atmospheric pressure the aldols decompose, partly into the constituent aldehydes from which they were produced, and partly into the corresponding unsaturated aldehyde (by loss of water).

ALDOSES *v.* CARBOHYDRATES.

ALE *v.* BREWING.

ALEMBROTH, SALT OF. A compound of mercuric chloride and sal ammoniac

$$2NH_4Cl,HgCl_2,H_2O$$

formed by mixing the two salts in suitable proportions. Also called by the alchemists Salt of Wisdom.

ALEUDRIN. Trade name for carbamic acid ester of αα-dichloro*iso*propyl alcohol.

ALEURITES CORDATA (Steud.). The seeds of this euphorbiaceous plant, which is found largely in Japan, yield Japanese wood-oil (*q.v.*).

ALEURITIC ACID *v.* LAC, Art. RESINS.

ALEURONE GRAINS. Organised granules deposited in the cells of many seeds of plants, generally near the exterior, in which the proteins are mainly concentrated. They were so named by Hartig, who first described them. In many plants, the aleurone grains possess the shape of crystals. Botanists, indeed, regard them as consisting of two parts: (1) a *crystalloid,* crystal-like protein body, and (2) one or more rounded *globoids* mainly composed of mineral matter, in which phosphoric acid, lime, and magnesia are usually the largest constituents.

When the aleurone grains exhibit the form of crystals, it is generally found that they are soft and swell up if treated with weak acids or alkalis. The term 'crystalloid,' as used by botanists in this connection, has reference to the appearance of the aleurone grains, and not to their property of diffusion when dissolved through membranes. According to Tschirch and Kritzler (Chem. Zentr. 1900, ii. 585), the aleurone grains of a variety of plants consist mainly of globulins. The crystalloids consist of at least two globulins, which are soluble in dilute, but insoluble in concentrated saline solutions (*e.g.* ammonium sulphate, sodium chloride with trace of acetic acid, potassium dihydrogen phosphate). A small amount of an albumose is also probably present. The globoids contain a globulin and mineral matter, especially calcium, magnesium, and phosphoric acid; they are soluble in concentrated solutions of ammonium sulphate, acidified sodium chloride, or potassium dihydrogen phosphate. The grains with their enclosures are reserve-food materials which are consumed when the seed germinates. They originate as liquid 'vacuoles,' in which an increasing amount of protein material is gradually deposited. The germinating power of seeds probably depends upon the solubility of the crystalloids in dilute sodium chloride solution.

According to Posternak (Compt. rend. 1905, 140, 322), aleurone grains often contain anhydro-oxymethylene diphosphoric acid, or inositol phosphoric acid $C_6H_6(PO_4H_2)_6$ (phytin). He found the following amounts of nitrogen and mineral substances in the aleurone grains of (1) spruce fir, (2) sunflower, (3) hemp, (4) white lupin:—

	N	K	Ca	Mg	Fe	Mn	P	S	Si
1.	12·97	2·50	0·37	1·25	0·09	0·25	2·67	0·64	0·35
2.	10·22	2·20	0·33	1·46	0·05	trace	2·78	0·64	0·24
3.	12·88	2·71	0·27	1·67	0·05	trace	3·83	0·81	0·36
4.	10·70	—	0·11	0·28	—	0·11	0·61	—	0·01

Sodium and chlorine were not found. H. I.

ALFA *v.* HALFA.

ALFALFA. The Spanish name for lucerne, *Medicago sativa* (Linn.).

ALFORMIN. A 16 p.c. solution of basic aluminium formate.

ALGÆ. (*Varech* or *Algues*, Fr.; *Algen*, Ger.). A class of cryptogamous plants including the green, brown, and red seaweeds and vegetable plankton growing in sea-water, and allied mainly green fresh-water plants, including diatoms, desmids, and 'conferva'-like forms. Many of the salt-water species are edible; none of them is poisonous.

Rhodymenia palmata (Linn.) (dulse, dylish, or dellish) and *Alaria esculenta* (murlins) are used as food by the peasantry of the Highlands and of Ireland. *Porphyra laciniata* (Lightf.) (laciniated purple laver), very abundant on the British coasts, is sold in England as laver, in Ireland as sloke, and in Scotland as slaak. *Chondrus crispus* (Linn.) (carrageen, Irish or pearl moss) is collected on the west coast of Ireland, and is frequently used there by painters and plasterers as a substitute for size. It is also used in making jellies, &c., in medicine;

and a thick mucilage scented with some prepared spirit is sold as 'bandolin,' 'fixature,' or 'clysphitique,' and is employed for stiffening silks.

Amongst other algæ having an economic value are Ceylon moss or edible moss (*Gracilaria lichenoides*), found in the Indian archipelago; the agar-agar of Malacca, or agal-agal of China, which is derived from *Gracilaria lichenoides*, *Eucheuma spinosum* (Linn.) and other algæ (*see* AGAR). The substance is now much used in bacteriological research as a nutrient jelly; for gumming silks, paper, &c., and for making a paste not liable to be eaten by insects.

Manna, or mannite, can be obtained from *Laminaria saccharina* (Lamx.) or sugar wrack, found on sandy shores, attached to pebbles.

In Yezo (Japan) different species of *Laminaria* and *Arthrothamnus* are collected for use as edibles, and in large quantities as raw material for iodine manufacture and potassium salts. Other varieties commonly used as a source of iodine are *Ecklonia cava* and *E. bicyclis*.

Alginic acid (Algin) is prepared from *Macrocystis pyrifera*, found on the Pacific coast of America, by treating a sodium carbonate extract with hydrochloric acid, redissolving in sodium carbonate and reprecipitating with acid several times, then dissolving again in sodium carbonate, purifying the sodium alginate by dialysis, decomposing it with hydrochloric acid, and purifying the alginic acid by dialysis. Alginic acid dried at 100° will absorb 200 to 300 times its weight of water. Its optical activity is $[\alpha]_D^{15\cdot5°} = 169\cdot2°$. The sugars produced by hydrolysis with 2 p.c. hydrochloric acid gave a yellow osazone, m.p. 154°-155°, closely resembling *l*-xylosazone, and also a red amorphous osazone.

Algin probably consists of a complex composed of compounds of the pentosan type and cellulose. It has weakly acid properties, and the sodium salt precipitates many metals from solution (Hoagland, J. Agric. Research, 1915, 4, 39; J. Biol. Chem. 1915, 23, 287. *See* IODINE.

The following table shows the composition of various species of algæ; the quantity of nitrogen in some of them is remarkably large:—

Alga	Water	Dry matter	Per cent. nitrogen in dry matter	Protein contained in dry matter
Chondrus crispus, bleached from Bewlay Evans .	17·92	82·08	1·534	9·587
Chondrus crispus bleached second experiment . .	19·79	80·21	1·485	9·281
Chondrus crispus, unbleached Ballycastle .	21·47	78·53	2·142	12·387
Chondrus crispus, unbleached, second experiment . . .	19·96	80·04	2·510	15·687
Gigartina mamillosa, Ballycastle . . .	21·55	78·45	2·198	13·737
Laminaria digitata, or dulse tangle . .	21·38	78·62	1·588	9·925
Rhodymenia palmata .	16·56	83·44	3·465	21·656
Porphyra laciniata . .	17·41	82·59	4·650	29·062
(*Sarcophyllis*) *edulis* .	19·61	80·39	3·088	19·300
Alaria esculenta . .	17·91	80·09	2·424	15·150

Certain of the *Laminaria*, after washing to remove salts, are found to be suitable as fodder, and when mixed with hay and straw in lieu of oats are readily eaten by horses. Although poorer in carbohydrates than oats the seaweed is much richer in protein.

In addition to the large amount of chlorine in marine algæ (up to 38 p.c. of the ash) there are often not inconsiderable quantities of iodine, the presence of which is responsible for the employment of seaweeds in the composition of certain 'anti-fat' specifics.

Certain algæ are characteristic of water containing sewage and putrefactive substances in quantity, and some algæ play an important *rôle* in the disinfection of polluted rivers.

ALGAROBILLA. Algarobilla consists of the pods of *Cæsalpina brevifolia*. The tannin, which appears to be a mixture of allagetannin and gallotannin, lies in semi-resinous particles adhering loosely to the somewhat open framework of the fibre. It is one of the strongest tannin matters known, and contains on the average 45 p.c. In character it resembles dividivi, and its extract is somewhat prone to fermentation. It is very suitable for tanning and also for dyeing purposes.

ALGAROTH, POWDER OF. *Pulvis Algarothi, English Powder.* A crystalline oxychloride of antimony, obtained by pouring antimony chloride into hot water. Used in the preparation of tartar emetic (*v.* ANTIMONY).

ALGARROBIN. A natural dye product, obtained from the wood of the carob tree, *Ceratonia siliqua*, found in the Argentine. According to a report of the United States Consul-General at Buenos Ayres, it is largely employed in the Argentine for dyeing khaki cloth for military purposes, and some quantity is also imported to the Continent of Europe. It is said to dye the textile fibres a light brown colour, though if these be previously mordanted, more varied shades may be obtained. As it acts also as a mordant for the coal tar colours, it would appear to be a tannin, and may be allied to ellagitannin, as its name suggests (*cf.* ALGAROBILLA, *l.c.*). A. G. P.

ALGIN. A nitrogenous body obtained from seaweed, somewhat resembling albumen (*v.* ALGÆ). Used in the sizing and finishing of certain textile fabrics as a substitute for Irish moss (carrageen); should contain from 4 to 6 p.c. of alginic anhydride (*v.* IODINE).

ALGIRON (*Alginoid iron*). Trade name for an iron compound of alginic acid (from seaweed); contains 11 p.c. iron.

ALGODONITE. A copper arsenide of a steel-grey colour. Found in the Lake Superior copper-mining district.

ALGOL COLOURS *v.* ALIZARIN AND ALLIED COLOURING MATTERS; VAT DYES.

ALGOLAVE. Trade name for the salicylic ester of propyl oxy*iso*butyric acid.

ALHAGI CAMELORUM (Fischer), **JAWASA, or JAWANI.** A leguminous thorny shrub, widely spread from Greece to dry parts of India, where a drug extracted from it is used for rheumatism, and also as a laxative and diuretic (Pharm. J. [3] 9, 145).

ALIVAL. Iodo hydroxypropane.

ALIZARIN AND ALLIED COLOURING MATTERS. *See* also articles on ANTHRACENE, ANTHRAQUINONE, CHAY ROOT MADDER, METHYL ANTHRACENE, VAT DYES. Madder, *Rubia tinctoria*, which was for a long time used on a large scale in the 'Turkey-red' industry, contains two colouring matters, alizarin and purpurin, of which the former is by far the more important.

Alizarin is not found ready-formed in the madder-root, but exists there as a glucoside called 'ruberythric acid,' which when allowed to ferment, or when boiled with dilute acid, splits up readily into alizarin and glucose.

The colouring matter itself was first isolated from the madder-root in 1827 by Colin and Robiquet, who obtained it by extracting ground madder with hot water and subliming the purified extract carefully in a glass tube.

This method of sublimation was not considered sufficient proof of the existence of alizarin in madder, and it was not till Schunck succeeded in isolating this substance by chemical means from the madder extracts used by dyers that this important point was definitely settled.

In assigning the correct formula to alizarin, considerable difference of opinion existed at first, owing no doubt to some extent to the difficulty experienced in obtaining alizarin in a condition pure enough for accurate analysis.

Schunck proposed the formula $C_{14}H_{10}O_4$, whilst Strecker believed it to be $C_{10}H_6O_3$ and related to 'chloroxynaphthalic acid' (chlorohydroxynaphthaquinone), a derivative of naphthalene, since both these substances on oxidation yield phthalic acid.

Strecker's formula was the more generally accepted by chemists, and chloroxynaphthalic acid was looked upon as being simply chlorinated alizarin, the two bodies being thus related:

$C_{10}H_6O_3$	$C_{10}H_5ClO_3$
Alizarin.	Chlorinated alizarin or Chloroxynaphthalic acid.

In order to prove the relation supposed to exist between these two substances, it was only necessary to replace the chlorine atom in chloroxynaphthalic acid by hydrogen, when alizarin should result.

This operation was eventually accomplished by Martius and Griess, who obtained thus a substance of the formula $C_{10}H_6O_3$, which was, however, not identical with alizarin, and was therefore supposed to be isomeric with it.

Following these experiments of Martius and Griess, Graebe, in 1868, commenced his research on quinones, the working out of which led not only to results which proved beyond a doubt what the chemical nature of alizarin really was, but also eventually resulted in the artificial production of this important colouring matter. In pursuing this investigation Graebe succeeded in preparing chloranil $C_6Cl_4O_2$, by treating phenol with potassium chlorate and hydrochloric acid, and in acting on this with caustic potash he found that two of the atoms of chlorine in this compound became replaced by (OK), producing the potash salt of chloranilic acid $C_6Cl_2(OK)_2O_2$, a change the knowledge of which proved to be of the utmost importance in his subsequent experiments on the artificial production of alizarin.

Chloroxynaphthalic acid was now considered by Graebe to be related to naphthalin in much the same way as chloranil was to benzene, *i.e.* to be a derivative of naphthaquinone.

Soon after this the attention of Graebe and Liebermann was turned to alizarin, which they also thought might belong to the quinone series.

In determining the constitution of this substance, the first step was to obtain some information as to the nature of the hydrocarbon from which alizarin was derived, and this was done in the following way: Alizarin prepared from madder was mixed with zinc-dust and heated strongly in a furnace, according to Baeyer's method of reducing benzenoid compounds, and in this way a crystalline hydrocarbon was obtained having the composition $C_{14}H_{10}$, which on examination was found to be identical with anthracene, a hydrocarbon previously obtained by Dumas and Laurent from coal tar. Using the information already obtained in the research on quinone, Graebe and Liebermann now assumed that alizarin must be a dihydroxyquinone of anthracene, the relation of these substances to one another being seen from the following formulæ:—

$C_{14}H_{10}$	$C_{14}H_8O_2$	$C_{14}H_6O_2(OH)_2$
Anthracene.	Anthraquinone.	Alizarin.

Having thus obtained anthracene from alizarin, it was now only necessary to reverse the operation and convert anthracene into alizarin, and the problem of the artificial production of a vegetable colouring matter would be solved for the first time.

In 1862 Anderson, while investigating anthracene, obtained from it by oxidation a substance of the formula $C_{14}H_8O_2$, which he named oxanthracene.

In this substance Graebe and Liebermann recognised the quinone of anthracene (anthraquinone), the first step in the synthesis of alizarin from anthracene, and in order to convert this quinone into alizarin all that was necessary was to replace two atoms of hydrogen in it by hydroxyl, an operation which is easily done in the following way:—

Anthraquinone when heated with two molecules of bromine in sealed tubes is converted into dibromanthraquinone, thus:

$$C_{14}H_8O_2+2Br_2=C_{14}H_6Br_2O_2+2HBr.$$

This substance when heated with potash exchanges each of its bromine atoms for (OK), yielding the potash salt of alizarin, $C_{14}H_6(OK)_2O_2$, a reaction which is precisely similar to the formation of chloranilate of potash from chloranil as described above. The potassium alizarate thus obtained, when decomposed with hydrochloric acid, yielded alizarin, and thus the problem of the artificial production of alizarin was solved.

In considering this synthesis, perhaps the most remarkable fact, from a chemical point of view, is that, in consideration of the number of possible isomers of alizarin, just that dibromanthraquinone prepared by Graebe and Liebermann should on treatment with potash have yielded alizarin. Had this not been so, the artificial production of alizarin would no doubt have been very much delayed.

The great importance of alizarin as a dyeing agent induced Graebe and Liebermann to patent this process, which proved, however, to be of no commercial value, owing to the great expense attending the use of bromine, and it was therefore desirable to find some new method which would render their discovery important from a manufacturing point of view.

This was first achieved by W. H. Perkin[1] in the following way:—Sulphuric acid, as is well known, forms with many organic bodies compounds called sulphonic acids, which in composition simply correspond to the substance acted on *plus* sulphuric anhydride.

Thus benzene C_6H_6 when treated with sulphuric acid yields benzenesulphonic acid $C_6H_5SO_3H$; naphthalene $C_{10}H_8$, naphthalenesulphonic acid $C_{10}H_7SO_3H$. When fused with caustic potash these sulphonic acids are split up into the potassium salt of the corresponding phenol and potassium sulphite, thus:

$$C_6H_5SO_3H + 3KOH = C_6H_5OK + K_2SO_3 + 2H_2O.$$

Similarly disulphonic acids when fused with potash are converted into dihydric phenols, thus:

$$C_6H_4(SO_3H)_2 + 6KOH = C_6H_4\begin{matrix}OK\\OK\end{matrix} + K_2SO_3 + 4H_2O.$$

In this second example it will be seen that a body is formed which bears the same relation to benzene as alizarin does to anthraquinone, and it was therefore probable that if anthraquinone were subjected to a similar series of reactions, alizarin would result.

The great obstacle to carrying out this synthesis, in the first instance, was the remarkable stability of anthraquinone in general and particularly towards sulphuric acid, which is so great that it dissolves in moderately hot sulphuric acid without change, and crystallises out again in needles on cooling.

When, however, a mixture of anthraquinone and sulphuric acid was heated very strongly, reaction did eventually take place, the product becoming perfectly soluble in water, the solution now containing mono- and disulphonic acids of anthraquinone.

After removing the excess of sulphuric acid from the new product, it was mixed with caustic potash, and heated to about 180°.

During the heating the melt became darker and darker in colour, and eventually almost black, and on dissolving this in water a rich purple solution was obtained which when acidified with dilute sulphuric acid gave a copious precipitate of alizarin.

The great obstacle to the preparation of alizarin—viz. the use of bromine—was thus removed, and, as the future has proved, a process had been obtained by which this colouring matter could be manufactured in quantity and at a price so cheap as entirely to supersede the old method of dyeing with the madder root.

Another process for the manufacture of artificial alizarin shortly afterwards discovered by W. H. Perkin, and largely used by him on a manufacturing scale, is the following:—

Anthracene is treated with chlorine and thus converted into a beautifully crystalline compound called dichloranthracene $C_{14}H_8Cl_2$.

This substance combines with Nordhausen sulphuric acid, forming a bright-green solution, which contains a sulphonic acid of dichloranthracene. When heated with sulphuric acid this substance undergoes a remarkable change, hydrochloric acid and sulphurous acid are evolved, and a disulphonic acid of anthraquinone formed, thus

$$\underset{\text{Dichloranthracene-disulphonic acid.}}{C_{14}H_6Cl_2(SO_3H)_2} + H_2SO_4 = \underset{\text{Anthraquinone disulphonic acid.}}{C_{14}H_6O_2(SO_3H)_2} + 2HCl + SO_2$$

This anthraquinone disulphonic acid when fused with potash yields alizarin.

Although other methods for the production of alizarin have since been devised, there is little doubt that the bulk of the alizarin of commerce is still obtained from 'silver salt,' the name given in the works to sodium anthraquinone-2-sulphonate.

Alizarin, purpurin and similar dyes will not dye unprepared fabrics; these must first of all be mordanted.

The mordants used in this case consist of metallic hydroxides—*e.g.* of aluminium, iron, and chromium. Chloride of tin (tin crystals) is also extensively employed.

With alumina mordants alizarin produces shades of red and pink; with iron mordants, shades of black and purple; with chromium mordants, a dull purple; and with tin crystals a bright yellowish orange. These mordants may also be mixed and thus a large variety of different shades produced. A description of the method of application of these various mordants and the processes employed in dyeing with alizarin will be found in the article DYEING.

Since the first production of artificial alizarin on the large scale, the study of this substance and of the various colouring matters related to it has received a large amount of attention at the hands of chemists, the result being that a considerable number of derivatives of anthraquinone have been prepared and examined.

Most of these are either colouring matters themselves, or easily converted into such, several of them being obtained on the large scale in the manufacture of alizarin.

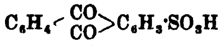
These derivatives may be divided under the following heads:—

(1) Sulphonic acids of anthraquinone.
(2) Monohydroxyanthraquinones.
(3) Dihydroxyanthraquinones.
(4) Trihydroxyanthraquinones.
(5) Higher hydroxylated anthraquinones.

In this article are included the two dyeing matters, Gallein and Cœrulein, which are very closely allied to alizarin in tinctorial properties, and also a brief description of some acid wool dyes derived from hydroxyanthraquinones.

Sulphonic acids of anthraquinone.

Anthraquinone-1- (or α-) sulphonic acid



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_3{\cdot}SO_3H \quad (1)$$

It is a remarkable instance of the influence of a catalyst that whilst anthraquinone ordinarily sulphonates in the 2- position, yet in the presence of quite small amounts of mercury the 1- position is almost exclusively attacked.

In preparing anthraquinone-1-sulphonic acid 100 parts of anthraquinone are heated for three hours at 130° with 110 parts of sulphuric acid, containing 29 p.c. sulphuric anhydride, and 0·5 part of mercury.

The free acid is easily soluble in alcohol and

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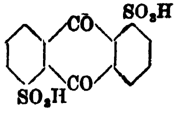
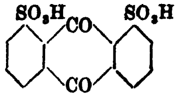
[1] It should be mentioned here that while these experiments were in progress, Caro, Graebe and Liebermann were investigating the same reaction in Germany.

water, its lead, barium, and strontium salts are very insoluble in hot water. The calcium salt is fairly soluble, but crystallises on heating the solution. The potassium salt occurs in glistening yellow leaflets.

Anthraquinone-1 : 5- and -1 : 8-disulphonic acids



and



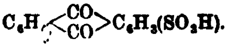
The further sulphonation of the α acid in presence of mercury leads to the formation of 1 : 5- anthraquinone disulphonic acid, mixed with 1 : 8- and 1 : 7- acids. The same mixture is produced by the direct sulphonation of anthraquinone (100 parts) with 200 parts of sulphuric acid containing 40 p.c. sulphur trioxide, in the presence of mercury (1 part) at 160° for one hour. The mixture of acids is converted into calcium salt and fractionally crystallised. The calcium salt of the 1 : 8- acid is least soluble, the middle fraction is the largest and consists of 1 : 5-, whilst the calcium salt of 1 : 7- is easily soluble.

Alternatively and preferably the acids may be separated by taking advantage of their different solubilities in sulphuric acid. The reaction mixture obtained in the above described preparation would be mixed with 100-200 parts of sulphuric acid (60° Be.), and the 1 : 5- acid is then obtained in the crystalline condition and collected on asbestos. The 1 : 8-isomeride is precipitated from the filtrate on the addition of half its volume of water. Both acids are converted into potassium salts by adding potassium chloride to their hot aqueous solutions. The success of these sulphonations depends very largely on the even distribution of the mercury catalyst throughout the mass, and to attain this end the mercury may be introduced in the form of yellow mercuric oxide, or a mercurous or mercuric salt, and intimately mixed with the anthraquinone employed in the operation. The discovery of a simple method of manufacture of these α-sulphonic acids of anthraquinone led to a great development in the anthracene series of dyes, especially in connection with the production of acid wool dyes of the type of Alizarin Saphirol, and a whole series of vat dyes, for example, the Algol colours (*see* VAT DYES).

The α-sulphonic acids may also be obtained by the oxidation of the sulpho-derivatives of anthracene. Thus anthracene α- and θ-disulphonic acids yield anthraquinone-1 : 8- and 1 : 5-disulphonic acids respectively on treatment with nitric acid. Chlorine or bromine atoms in the alpha position in the anthraquinone nucleus may be displaced in favour of the sulpho-group by treatment of these halogen derivatives with aqueous sodium sulphite. Neither of these methods possesses technical importance.

Literature.—Liebermann and Dehnst (Ber. 12, 1288), Iljinsky (Ber. 36, 4194), Schmidt (Ber. 1904, 37, 66; Eng. Pat. 10242 and 13808, 1903; D. R. P. 157123, 164292, and 167169), Cain (Intermediate Products for Dyes, Macmillan, 1918, 243).

Anthraquinone-2- (or β-) sulphonic acid



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_3(SO_3H).$$

This acid is formed together with a certain amount of anthraquinone disulphonic acid by heating anthraquinone with fuming sulphuric acid to 170° or with ordinary sulphuric acid to 250°-260°.

In preparing it a mixture of one part of fuming sulphuric acid (containing 40–50 p.c. anhydride) and 1–1½ parts of anthraquinone is gradually heated to about 160° and kept at this temperature for eight or ten hours, the whole being well stirred during the operation.

The product thus formed consists chiefly of the monosulphonic acid together with a little disulphonic acid and unchanged anthraquinone. On diluting with water the anthraquinone separates out, and can easily be filtered off, leaving the sulphonic acids in solution. In order to separate the mono- from the disulphonic acid the clear filtrate is neutralised with carbonate of soda (or caustic soda). This causes the difficultly soluble sodium salt of anthraquinone monosulphonic acid to separate out, leaving the easily soluble salt of the disulphonic acid in solution.

The pasty mass obtained on neutralising with soda is thoroughly pressed, washed with a little water, and then if required pure recrystallised from this solvent. In this way a beautiful brilliant white scaly crystalline mass is obtained, which consists of pure sodium anthraquinone monosulphonate, the so-called 'silver salt' of the alizarin manufacturer. This salt crystallises with $1H_2O$, and 100 parts of water dissolve 5·59 parts at 18°, and 18·88 parts at 100°.

The free acid obtained by the addition of an acid to the soda salt crystallises in plates. It is very easily soluble in cold water and alcohol, but almost insoluble in ether.

Dünschmann has pointed out that acids other than the β-acid are obtained in this process and that, after the greater part of the 'silver salt' has separated, further concentration gives a product containing the two monosulphonic acids of anthraquinone mixed with the 2 : 6-disulphonic acid. The final mother liquor contains the 2 : 7-disulphonic acid. A hot saturated solution of the mixed acids is treated with one-tenth of its volume of a 45 p.c. solution of sodium hydroxide and cooled to 55°–60°, whereupon most of the 2 : 6-acid separates as sodium salt, whilst on cooling the mother-liquor sodium anthraquinone-1-sulphonate crystallises. To avoid the formation of these by-products Grandmougin employs as sulphonating agent an acid containing only 15 p.c. SO_3 at 150°, and under these conditions it is stated that only the β-acid is produced.

When fused with caustic soda, this acid (or rather its sodium salt) gives first hydroxyanthraquinone $C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_3OH$, and then alizarin; and, as will be shown later on, alizarin, when prepared on a manufacturing scale, is invariably formed from the monosulphonic acid of anthraquinone, not from the disulphonic acid as might be expected. The reason for this is that on fusing hydroxyanthraquinone with caustic soda, a continuous process of oxidation and reduction is carried on, the change being represented by the following equation:—

$$C_{14}H_7(ONa)O_2+NaOH+O$$

Sodium monohydroxyanthraquinonate.

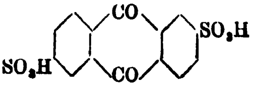
$$=C_{14}H_6\begin{pmatrix}ONa\\ONa\end{pmatrix}O_2+OH_2$$

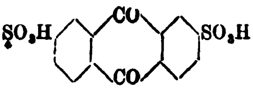
Sodium alizarate.

the oxygen being supplied at the expense of a part of the hydroxyanthraquinone which is thereby reduced to anthraquinone. On the large scale this reduction is prevented by the use of chlorate of potash in the fusion.

Literature.—Graebe and Liebermann (Annalen, 160, 131; 212, 44; Ber. 7, 805); Grandmougin (Lehrbuch der Farben Chemie, 4th ed. 1913, 260); Dünschmann (Ber. 37, 321).

Anthraquinone-2 : 6- and 2 : 7-disulphonic acids (α- and β-disulphonic acids respectively),





In the presence of the mercury catalyst anthraquinone-2-sulphonic acid is attacked in the positions 5 and 8, yielding anthraquinone-1 : 6- and 1 : 7-disulphonic acids, the constitutions of which have been proved by conversion into the corresponding hydroxyanthraquinones by heating under pressure with milk of lime. On the other hand, sulphonation, in the absence of mercury, of either anthraquinone or its β-sulphonic acid, yields a mixture of the 2 : 6- and 2 : 7-acids. The higher the temperature the greater the proportion of the α- or 2 : 6-acid which is formed.

(1) A mixture of 10 kilos of anthraquinone and 20 to 30 kilos of fuming sulphuric acid, containing 45–50 p.c. SO_3, is heated to a temperature of 160°–170° until a sample taken out is found to dissolve completely in water. The product is then heated another hour to convert any mono- into disulphonic acid, poured into water, neutralised with caustic soda, and evaporated.—(2) 10 kilos of anthraquinone, 12 kilos of hydrogen sodium sulphate, and 40 kilos of ordinary concentrated sulphuric acid are heated under pressure for five or six hours to 260°, the product treated with water, and the acids converted into sodium salts as above.

In concentrating the solution of the sodium salt obtained by either of the above methods, the sodium salt of the α-acid crystallises out first, the more readily soluble salt of the β-acid remaining in the mother-liquors, and thus by repeated recrystallisation, the two acids are easily separated from one another.

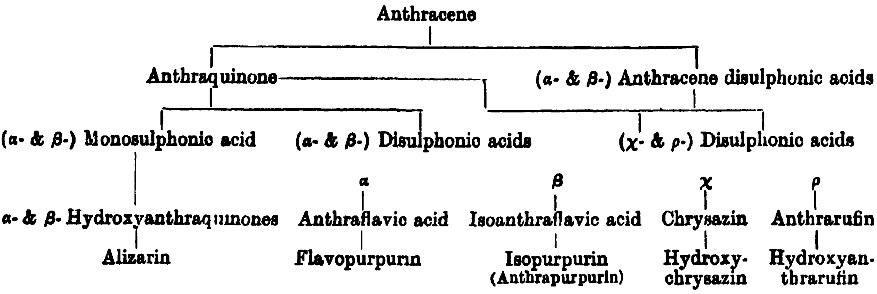
The free acids obtained by decomposing the salts by an acid are both readily soluble in alcohol and water, but insoluble in ether and benzene; the α-acid crystallises in small yellow crystals, the β-acid in beautiful yellow plates.

The salts of the α-acid are sparingly soluble in water and crystallise with difficulty; those of the β-acid are readily soluble and crystallise with the greatest ease.

The sodium salt of the α-acid crystallises with $7H_2O$, that of the β-acid with $4H_2O$.

Literature.—Schultz (Chemie des Steinkohlentheers, 709, 712); Perkin (Chem. Soc. Trans. 1870, 133); Graebe and Liebermann (Annalen, 160, 134); Crossley (J. Amer. Chem. Soc. 1915, 37, 2178).

The relation of the various colouring matters of this group to anthracene, anthraquinone, and its sulphonic acids is easily understood from the following table (Schultz):—


Anthracene
Anthraquinone
(α- & β-) Anthracene disulphonic acids
(α- & β-) Monosulphonic acid
(α- & β-) Disulphonic acids
(χ- & ρ-) Disulphonic acids
α
β
χ
ρ
α- & β- Hydroxyanthraquinones
Anthraflavic acid
Isoanthraflavic acid
Chrysazin
Anthrarufin
Alizarin
Flavopurpurin
Isopurpurin (Anthrapurpurin)
Hydroxychrysazin
Hydroxyanthrarufin

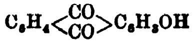
The behaviour of the anthraquinone disulphonic acids on fusion with potash is exactly similar to that of the monosulphonic acid. Just as this acid on fusion with potash is first converted into monohydroxyanthraquinone and then by oxidation into dihydroxyanthraquinone (alizarin), so the anthraquinone disulphonic acids in the first place yield the corresponding dihydroxyanthraquinones, which then by the further action of the potash are converted into trihydroxyanthraquinones.

The sulphonic acids of anthraquinone are important intermediates apart from their conversion into the various hydroxy derivatives. The sulphonic group may be displaced by amino, alkylamino-, and arylamino- groups, usually by treatment with ammonia or an amine at a high temperature and occasionally in the presence of a copper compound, sodium carbonate, or an oxidising agent. Moreover, the chloro- derivatives of anthraquinone are most conveniently prepared by the action of sodium chlorate on a solution of an anthraquinone sulphonic acid in dilute hydrochloric acid at

90°-100°. For example, 1 : 5-dichloroanthraquinone used for the manufacture of Indanthrene Violet R.N. is obtained in this way from anthraquinone-1 : 5-disulphonic acid (D. R. P. 205195).

Hydroxyanthraquinones.

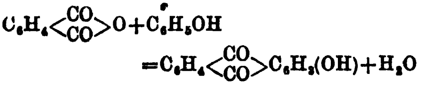
I. Monohydroxyanthraquinones



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_3OH$$

1- Hydroxyanthraquinone. Erythroxyanthraquinone.

This substance is formed together with 2-hydroxyanthraquinone by strongly heating a mixture of phenol and phthalic anhydride with sulphuric acid



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}O+C_6H_5OH$$
$$=C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_3(OH)+H_2O$$

Also by heating 1-bromanthraquinone with potash to 160° or by acting on 1-amidoanthraquinone with nitrous acid in concentrated sulphuric acid solution.

The most satisfactory method of preparation consists in heating anthraquinone-1-sulphonic acid with water and an oxide, or hydroxide of an alkaline earth metal under pressure.

1-Hydroxyanthraquinone crystallises from alcohol in orange-red needles which melt at 190°. When fused with potash it gives alizarin. The substance does not dye mordanted fabrics.

1-Acetoxyanthraquinone, prepared by boiling erythroxyanthraquinone with acetic anhydride and sodium acetate, crystallises in yellow needles from alcohol and melts at 176°-179°.

1-Methoxyanthraquinone is obtained by the action of boiling methyl alcoholic potash on 1-nitroanthraquinone.

This is the simplest example of a very general reaction in the anthraquinone series. The substance is yellow, microcrystalline, and melts at 140°-145°.

Literature.—Baeyer and Caro (Ber. 7, 969); Pechmann (Ber. 12, 2128); Römer (Ber. 15, 1793), Liebermann and Hagen (Ber. 15, 1804); Hoechste Farbwerke (D. R. P. 97688).

2- Hydroxyanthraquinone.

This substance is obtained synthetically (together with erythroxyanthraquinone) by heating a mixture of phenol, phthalic anhydride, and sulphuric acid. The mixed hydroxyanthraquinones can be separated by means of baryta water, since the barium salt of 1- hydroxyanthraquinone is insoluble, whilst the 2- hydroxy compound is easily soluble. It crystallises from alcohol in yellow plates which melt at 323° and readily sublimes at a higher temperature.

It can be obtained in various ways from anthraquinone or its derivatives.

An easy preparation consists in melting anthraquinone sulphonic acid or 2- bromanthraquinone with potash.

The action of ammonium persulphate on a solution of anthraquinone in concentrated sulphuric acid containing sulphur trioxide leads to the production of 2-hydroxyanthraquinone, alizarin, and purpurin.

Alizarin is reduced to 2-hydroxyanthraquinone by the action of alkaline stannous chloride; or alizarin amide, obtained by the action of ammonia on alizarin, yields this substance when treated with ethyl nitrite.

A very curious reaction of this hydroxyanthraquinone, and one which involves migration of an oxygen atom, is its conversion to quinizarin by treatment with nitrous acid in sulphuric acid solution and in the presence of boric acid.

Literature.—Graebe and Liebermann (Annalen, 160, 141); Baeyer and Caro (Ber. 7, 969); Liebermann and Fisher (Ber. 8, 975); Liebermann (Annalen, 183, 208); Wacker (J. Pr. Chem. [2] 54, 89); Bayer & Co. (D. R. P. 86830).

Dihydroxyanthraquinones.

Alizarin

1 : 2-dihydroxyanthraquinone

$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_2(OH)_2.$$

Alizarin occurs in madder as the glucoside ruberythric acid, and also in Chay root (*Oldenlandia umbellata*) and some species of rhubarb.

It is obtained from its glucoside by the action of dilute acids or of ferments.

$$\underset{\text{Ruberythric acid.}}{C_{26}H_{28}O_{14}} + 2H_2O = \underset{\text{Alizarin.}}{C_{14}H_8O_4} + \underset{\text{Glucose.}}{2C_6H_{12}O_6.}$$

It may be prepared artificially by many methods.

Thus alizarin is produced by fusing dichloranthraquinone, dibromanthraquinone, anthraquinone, mono- or di-sulphonic acids with potash. Rufigallic acid yields alizarin when reduced with sodium amalgam.

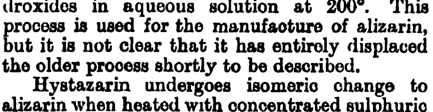
On the other hand, anthraquinone may be directly oxidised to alizarin by the action of ammonium persulphate in concentrated sulphuric acid solution.

Good yields of alizarin are said to be obtained by heating anthraquinone with sodium chlorate and a mixture of sodium and potassium hydroxides in aqueous solution at 200°. This process is used for the manufacture of alizarin, but it is not clear that it has entirely displaced the older process shortly to be described.

Hystazarin undergoes isomeric change to alizarin when heated with concentrated sulphuric acid to 200° for two and a half hours.

Alizarin may be synthesised by processes not involving the intermediate formation of anthraquinone.

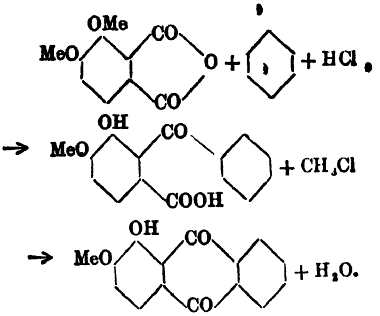
Together with hystazarin it is produced when a mixture of catechol and phthalic anhydride is heated with sulphuric acid at 200°.



$$\underset{\text{Phthalic anhydride.}}{C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}O} + \underset{\text{Catechol.}}{C_6H_4(OH)_2}$$
$$=\underset{\text{Alizarin.}}{C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_2(OH)_2 1:2} + H_2O.$$

A method somewhat similar in principle is the following :—

Hemipinic anhydride condenses with benzene in the presence of aluminium chloride, yielding the methyl ether of dihydroxybenzoylbenzoic acid. This latter substance, on treatment with hot sulphuric acid, is converted into alizarin methyl ether, which is hydrolysed by aluminium chloride to alizarin. The following formulæ represent this series of reactions :—



Alizarin methyl ether.

Lagodzinski has converted 1 : 2-anthraquinone into alizarin by reducing this *o*-quinone to 1 : 2-dihydroxyanthracene, the diacetyl derivative of which yields diacetylalizarin on oxidation with chromic acid in acetic acid solution. The diacetate is then hydrolysed.

Finally, alizarin is frequently formed in relatively small proportion in the reduction of 1-nitroanthraquinone, for example, by means of sodium sulphide.

MANUFACTURE OF ALIZARIN.

1. *Anthraquinone process.*—Anthracene, the basis of alizarin, is obtained entirely from the coal-tar oils boiling above 300°, the so-called 'last runnings' of the tar distiller. These heavy oils are redistilled and the anthracene oils collected as soon as the distillate on cooling commences to solidify. In this way a semi-solid greenish-looking mass is obtained, which, after roughly freeing from excess of oil by treatment in hydraulic presses, is the starting-point in the alizarin factory. This crude product contains only about 30–40 p.c. anthracene, the remainder consisting of phenanthrene, naphthalene, carbazol, and small quantities of other hydrocarbons.

The first operation necessary in the manufacture of alizarin is that of purifying the crude anthracene obtained from the tar distillers, in order to obtain a product fit for the subsequent oxidation to anthraquinone.

This process of purification varies considerably in different countries, but the following method may be given as having been used with much success.

The crude anthracene is first ground between edge-runners, and then thoroughly agitated with boiling petroleum spirit in large iron vessels fitted with stirrers and heated with steam.

About 1500 to 1800 lbs. of crude anthracene and 300 gallons of petroleum spirit are used in one operation, the amount of the latter varying slightly according to the quality of the anthracene employed. After boiling for an hour or two, the product is allowed to cool, filtered through coarse canvas, and the anthracene on the filter washed with a little clean petroleum spirit. The pasty mass thus obtained is next treated with steam to remove the excess of petroleum spirit, and then sublimed. The sublimation process is best carried out by melting the anthracene in an iron pot, called the 'subliming pot,' and then blowing in superheated steam. This carries the anthracene vapour forward through a long pipe, where it meets a spray of water, which serves to condense both it and the steam. The anthracene is thus obtained in an extremely finely divided state, much more suitable for oxidation than when simply ground under edge-runners as it used to be. Another process of purification of anthracene consists in washing in a neutral solvent, such as coal tar naphtha, with concentrated sulphuric acid. This treatment removes the basic impurities, and the anthracene is further purified by sublimation. The next step consists in converting the anthracene into anthraquinone by oxidation with bichromate of potash (or soda) and sulphuric acid—an operation which is usually done in the following way:—The anthracene is placed in lead-lined tanks with about twice its weight of the bichromate (dissolved in water), the requisite amount of dilute sulphuric acid is slowly added, and the mass kept well boiled and agitated by a steam jet connected with a Körting's injector.

The whole is then transferred to settling tanks, the crude yellowish-brown anthraquinone well washed by decantation until free from green chrome liquors, well drained, and freed from water as completely as possible by placing it in canvas bags and exposing it to great pressure in a hydraulic press. The amount of oxidiser required to convert the crude anthracene into anthraquinone is of course regulated by the purity of the sample employed, pure anthracene requiring about 1·66 times its weight of potassium bichromate to convert it into anthraquinone.

Instead of potassium bichromate, the sodium salt is now very often used on account of its cheapness.

The anthraquinone thus obtained is still very impure, and must be carefully purified before it can be converted into sulphonic acid. In purifying anthraquinone two methods may be employed:

(1) The anthraquinone is sublimed, and then, if necessary, recrystallised from high boiling coal-tar naphtha.

(2) The anthraquinone is treated with concentrated sulphuric acid.

When the first process is employed, the anthraquinone is melted in iron pots and subjected to the action of super-heated steam. The steam carries the vapour of the anthraquinone with it, and on condensation a fine, almost impalpable powder is obtained, which, when dried and recrystallised from high-boiling coal-tar naphtha, consists of nearly pure anthraquinone.

In this country this process has now been almost abandoned; method (2) having entirely taken its place.

The working of this method is based on the fact that crude anthraquinone when treated with sulphuric acid at 100° dissolves, but is not acted on. The impurities, however, become converted into sulphonic acids, which, being easily soluble, can be removed by treating the product with water, when nearly pure anthraquinone is left behind.

In carrying out this operation a mixture of 1 part of crude anthraquinone and 3 parts of sulphuric acid is placed in large circular lead-lined iron pots, and heated by steam for twenty-four hours, the whole being continuously agitated by a stirrer.

The blackish-looking product is then run into shallow tanks, and exposed to the action of damp air, or a gentle current of steam, until the acid has become diluted. In a short time anthraquinone separates out as a light-brown crystalline powder, which, after washing by dilute soda and by decantation, pressing, and thoroughly drying, is found to contain about 95 p.c. of pure substance.

According to recent patents anthraquinone is best purified by crystallisation from liquid sulphur dioxide or from aniline.

The following account of the manufacture of anthraquinone is given by Cain (Manufacture of Intermediate Products for Dyes, p. 235) as an abstract of a communication by Grandmougin (Rev. prod. chim. 1917, 20, 20):—'The oxidation is effected in lead-lined tubs of about 10–12 cubic metres' capacity (about 2500 gallons), fitted with lead-covered agitators and direct steam pipes, also of lead. 150 kilos of sublimed anthracene are mixed with 3000–4000 litres of water, and the mixture is heated at 75°; 2000 litres of a solution containing 300 kilos of sodium dichromate and 600 kilos of sulphuric acid (66° Be.) are now run in slowly, the temperature being gradually raised to about 95°. The oxidation requires twelve to sixteen hours, and it is important not to add the chromic acid solution too quickly or to work in a too concentrated solution, otherwise much frothing occurs.

'Tests are made by filtering a sample, washing, and subliming it over a naked flame. With a little practice it is easy to distinguish the fine needles of anthraquinone from the silvery leaflets of anthracene. The absorption of the chromic acid can also be ascertained by titration with ferrous sulphate. When the operation is finished, the contents of the tub are run into an egg and blown through a filter press, where the anthraquinone is thoroughly washed, the filtrate being collected in order to recover the chromium. The yield from an anthracene of good quality is about 110 parts of anthraquinone from 100 parts of anthracene. The anthraquinone so obtained is purified by sublimation with super-heated steam; the pan is heated by super-heated water and the sublimed anthraquinone condensed by means of a water jet.'

Other processes for the oxidation of anthracene have been suggested but have not yet displaced the chromic acid method. A brief summary of these methods may be appended:—

(1) Oxidation of anthracene by oxides of nitrogen and air or oxygen alone or in the presence of various catalysts or substances capable of absorbing the oxides of nitrogen. Occasionally the anthracene is mixed with neutral substances, such as powdered glass or pumice. In one process anthracene is added to a solution of nitrogen peroxide in nitrobenzene and the temperature gradually raised to 100°. Anthraquinone is formed, and the nitric oxide is recovered and converted into peroxide for use in a further operation.

(2) Oxidation of anthracene by nitric acid. This is usually carried out in nitrobenzene solution and sometimes in the presence of mercuric nitrate.

(3) Oxidation of anthracene by means of sodium nitrate in the presence of magnesium chloride between 125° and 145°.

(4) Oxidation of anthracene by oxygen in the presence of aqueous ammonia and copper oxide at 170°. Nickel, cobalt, iron, and lead compounds may be used as catalysts instead of copper oxide.

(5) Electrolytic oxidation of anthracene may be carried out in a chromic acid bath or in 20 p.c. sulphuric acid solution in the presence of cerium sulphate.

(6) Oxidation of anthracene by means of ozonised air. In this case the hydrocarbon is dissolved in sulphuric acid.

(7) Oxidation of anthracene by means of a chlorate in aqueous solution in presence of an iron salt.

The following patents deal with the oxidation of anthracene: Eng. Pats. 5539, 1892; 17635, 1901; 759, 1882; 19178, 1902; 8431, 1887; 16312, 1909; 11472, 1910; 12055, 1914; 5514, 1915. Fr. Pats. 220621, 149017, 328069, 416735, 472216. U.S. Pats. 729502, 757136, 1083051, 1103383, 1119546. Ger. Pats. 68474, 137495, 21681, 109012, 152063, 215335, 207170, 234289, 254710, 256623, 268049; Anm. H 61262, 292681.

The next stage in the manufacture of alizarin is the conversion of anthraquinone into its sulphonic acid.

This operation, which consists in heating anthraquinone with fuming sulphuric acid, is conducted in large iron pots capable of holding from 30 to 40 gallons. The amount of fuming sulphuric acid employed depends on the nature of the sulphonic acid required. In preparing the monosulphonic acid, 1 part of fuming acid (contained 40–50 p.c. SO_3) and 1 to 1¼ parts of anthraquinone are used.

The mixture is gradually heated by means of an oil-bath to 170°, or even to 190°, and kept at this temperature for eight or ten hours, the stirrer being kept constantly in motion.

The product, which contains, besides anthraquinonemonosulphonic acid, a little disulphonic acid, and some unacted-on anthraquinone, is diluted with water, passed through a filter-press to remove the anthraquinone, and neutralised with caustic soda.

In a short time the whole becomes quite thick owing to the separation of the sparingly soluble soda salt of anthraquinonemonosulphonic acid, the easily soluble salts of the disulphonic acids remaining in solution.

The crystalline salt is collected in filter-presses, washed with a little very dilute sulphuric acid, and thus obtained practically pure in beautiful, brilliant, pearly scales.

In preparing the disulphonic acids of anthraquinone, the operation is similar to the above, the only difference being that more fuming sulphuric acid is used and the sulphonation conducted at a much higher temperature (about 260°).

The next operation consists in the conversion of the product just described, and called 'soda salt,' into colouring matter, a change which is accomplished by heating it strongly with caustic soda and a little potassium chlorate.

If the potassium chlorate is not added, a considerable loss is incurred owing to the reducing action of a large quantity of nascent hydrogen, always formed during the fusion, which converts the soda salt partially into anthraquinone and hydroanthraquinone. The fusion is conducted in large wrought-iron cylinders fitted with stirrers and heated with hot air. The usual charge is 700 lbs. caustic soda (70 p.c.) dissolved in water, 1300 lbs. of a concentrated solution of 'soda salt,' and 13 to 15 p.c. of potassium chlorate, the amount of this latter substance varying slightly with the nature of the salt used, the monosulphonic salt requiring more chlorate than the disulphonic salt.

The temperature is maintained at about 180° for at least twenty-four hours and often much longer, the progress of the decomposition being controlled from time to time by extracting small quantities of the melt and examining them in the laboratory.

The product thus obtained is an intense purple fluid, becoming thick on cooling and containing the colouring matter as sodium salt besides sodium sulphite and an excess of caustic soda.

To separate the colour the melt is run into large wooden tanks, diluted with water, and boiled with dilute sulphuric acid.

This causes the solution to become orange in colour owing to the precipitation of artificial alizarin.

After being allowed to settle, the supernatant liquor is run off, the alizarin forced into filter-presses and carefully washed until free from acid and saline matter. The colouring matter is then made up to a definite strength (10 p.c. or 20 p.c. paste as required) by transferring it to large wooden tubs fitted with powerful stirrers, and thoroughly mixing it with water.

Pure alizarin thus prepared produces a blue shade of Turkey-red, and anthrapurpurin (produced by fusing sodium anthraquinonedisulphonate with caustic soda) a red shade, so that by varying the amounts of these two constituents any intermediate shade required by the market can be obtained.

The foregoing may be now supplemented by a description of the manufacture of alizarin which is given by Ullmann. The sulphonation of anthraquinone is carried out in acid-resisting cast-iron vessels heated by super-heated steam. The pots have a diameter of 1165 mm., and height of 1235 mm., and are surmounted by covers which are fitted with a manhole, stirrer, pipe for introducing pressure, plunging tube for thermometer, and a contrivance for the automatic registration of temperature. 300 kilos of sublimed anthraquinone and 200 kilos of recovered quinone (the portion of the substance which is recovered from the sulphonations) are mixed with 400 kilos of oleum (20 p.c. SO_3) and 200 kilos oleum (60 p.c. SO_3), and the mixture heated at 145° during eight hours. This procedure may be modified by introducing half the amount of acid and heating four hours, after which the remainder is introduced during three hours more, and in one or two portions. Before the reaction mass cools it is forced into a lead-lined vat containing 1·5–2 cbm. water with continuous stirring. Further dilution to 5 cbm. is then made, and the mixture heated by the introduction of steam. Between 80 and 120 kilos of anthraquinone remain unattacked and are recovered by filtration through a press. The filtrate is mixed with 85 kilos caustic soda an amount which still leaves the liquor strongly acid, being only about three-eighths of that theoretically required for neutralisation. The difficultly soluble 'silver salt' separates, and is collected in a press. The filtrate is submitted to vacuum evaporation to 22°–23° Bé. (measured while hot), and underneath the evaporator there is a vat provided with stirring apparatus, and into which the liquor is allowed to run for crystallisation. The process is facilitated by providing the vat with a double jacket for cooling. The 'silver salt' is collected in a filter press and washed with brine, in which it is sparingly soluble. The yield of dry salt amounts altogether to 450–500 kilos. It requires no further purification for the preparation of alizarin of bluish shade. The mother-liquor from the monosulphonate is neutralised with lime, and the gypsum separated, after which the calcium salts are converted into sodium salts by means of sodium carbonate and the solution again filtered from chalk. Evaporation yields the 2 : 6- isomeride, and finally the 2 : 7-, but it is perhaps more usual to blow the concentrated mixture directly into the alkali fusion apparatus. The fusion of silver salt with alkali is carried out in a series of horizontally placed cylinders provided with stirring gear and heated by means of super-heated steam. They have to be capable of resisting a pressure of 12 atmospheres. The capacity is about 3550 litres, and they are about 2000 mm. long and have an inside diameter of 1400 mm. The following example of a fusion may be regarded as typical; 1687 cbm. of caustic soda solution (45° Bé.) containing 1030 kilos NaOH, together with 125 kilos saltpetre, are introduced into the pot and heated to about 125°, after which 625 kilos of moist silver salt (66·4 p.c.), corresponding to 415 kilos of the dry substance, are gradually added. The temperature is then raised to 180°, and the pressure reaches 4–4·5 atmospheres. After 36–48 hours the process is usually complete. This is confirmed by testing a sample by boiling with milk of lime, filtering from the sparingly soluble calcium alizarate and acidifying the filtrate, when an incomplete operation is indicated by the separation of golden flakes of oxyanthraquinone. The melt is diluted down to 6° Bé. in large lead-lined tanks, and acidified at 60° with sulphuric acid. For alizarin of especially blue shade the diluted alkali fusion melt is treated in boiling solution with milk of lime until a drop of the liquid placed on filter-paper gives a clear red rim. The calcium salt is then separated and decomposed with hydrochloric acid. The precipitated alizarin is collected in filter presses and washed until the filtrate is free from acid. The press-cakes are analysed for content of anhydrous ash-free alizarin, and on the basis of the analysis a 20 p.c. paste is made in a special mixer made of pitch pine. The paste has a thin appearance, but if it should be desired thicker it suffices to add 0·5–1 p.c. of salt. The thickening of the paste which follows is a most singular phenomenon, and resembles in appearance the salting out of a dye although, of course, the suspended solid is not increased in amount. For some Eastern markets a still thicker paste is prepared by the addition of glycerin, dextrin, molasses, or starch. Alizarin in lumps of such a character that paste may be prepared from them as desired is made by mixing 20 p.c. paste with starch, and then filtering off and very carefully and gradually drying the mixture. As much water as possible is removed by pressure, and the remainder in a vacuum at a temperature not exceeding 60°. During the whole process of alizarin manufacture it is most important that the water used should be soft and as free as possible from iron. Iron in the water will absolutely ruin the value of a batch of alizarin from the point of view of purity of shade. If through some defect in the apparatus a batch should become contaminated it is useless to attempt to purify the dye by solution in alkali, and reprecipitation with acid in view of the circumstance that the objectionable iron derivatives (*cf.* the alizarinferrates below) are reprecipitated along with the colouring matter. The best treatment is with hot dilute hydrochloric acid and just sufficient potassium chlorate to produce a clear yellow colour.

2. *Dichloranthracene process.*—In manufacturing alizarin by this process, which appears to have been abandoned in favour of that already described, it is necessary, in the first place, to purify the anthracene used much more thoroughly than is the case in the anthraquinone process.

For this purpose the anthracene, after washing with petroleum spirit as described in the last process, is submitted to distillation with potash. This removes the carbazol and the phenolic substances present in the crude anthracene, and as, besides this, a considerable quantity of the other impurities are charred during the distillation, the anthracene resulting, although still very impure, is found to be greatly improved in quality.

In carrying out this operation 100 parts of washed anthracene, 30 parts of potash, and 6 parts of powdered lime are thoroughly ground together under edge-runners, the mixture introduced into iron retorts and distilled. The distillate, which consists of pale-yellow cakes containing about 50 p.c. of pure anthracene, is now sufficiently pure for conversion into dichloranthracene.

In chlorinating anthracene, leaden chambers are used, technically known as 'chlorine ovens.' These are 10 ft. long, 4 ft. 6 in. wide, and 1 ft. 6 in. deep, and are used in pairs, connected at one end in order that any chlorine escaping from the first oven may come in contact with a fresh amount of anthracene and thus prevent loss.

400 lbs. of anthracene are put into each oven, and subjected to the action of a rapid current of chlorine for about five or six hours.

The anthracene first fuses and gets dark in colour, hydrochloric acid being evolved in abundance; but after a time this fluid product begins to deposit crystals and soon becomes a semi-solid mass. In order to purify this crude product, it is first freed from hydrochloric acid by washing with dilute caustic soda, and then pressed between linen cloths in a hydraulic press, by which means a considerable quantity of a thick dark oily product, technically known as 'chlorine oils,' is got rid of.

The yellow cakes of dichloranthracene thus obtained are still not pure enough for use; they must next be soaked in coal-tar naphtha for some time and pressed, this operation being repeated until a product is obtained which contains 84 p.c. of pure substance.

The next process consists in converting the dichloranthracene into the sulpho- acids of anthraquinone by treating it with ordinary concentrated sulphuric acid. This decomposition is accomplished in iron pots capable of holding about 30 gallons and fitted with iron covers in which there is an opening for the escape of the acid vapours formed during the reaction.

These pots are charged with 350 lbs. of concentrated sulphuric acid and heated to 140°–160° by means of an ordinary fire, the dichloranthracene (70 lbs.) being shovelled in in small quantities at a time. After all the dichloranthracene has been added and the frothing due to the evolution of the hydrochloric and sulphurous acids produced during the decomposition has subsided, the temperature is gradually raised to 260° and then maintained at this point until a sample taken out on a glass rod and diluted with water forms a nearly clear solution devoid of fluorescence.

The product contains now the mono- and disulphonic acids of anthraquinone, the latter of which greatly predominates.

These crude sulphonic acids are next diluted with water in a large wooden tank and boiled with slaked lime until neutralised. The neutral product is then forced into filter presses to separate the calcium sulphate, the clear filtrate mixed with the washing of the calcium sulphate, evaporated until it contains about 15 p.c. of lime salts, and then treated with sufficient sodium carbonate to precipitate all the lime as carbonate.

The solution of the sodium salts of the sulphonic acids is siphoned from the precipitated calcium carbonate, concentrated until it contains 30 p.c. of soda salts, and then converted into colouring matter by fusion with caustic soda, as described in the last process.

3. *Direct conversion of anthraquinone into alizarin.*—In the preparation of anthraquinone-β-sulphonic acid it is very difficult to avoid the production of some disulphonic acid, and even if the alizarin is purified as described below, the shades obtained on mordanted fabrics are not quite identical with those given by the chemically pure dyestuff. The Badische Anilin und Soda Fabrik claim (D. R. P. 116526) that a remarkably pure alizarin dyeing bluish shades of alizarin red on the usual alumina mordant may be prepared from anthraquinone under the following conditions:—Anthraquinone (100 parts) is heated with a solution of sodium or potassium hydroxide (300 parts) and sodium chlorate (20–30 parts) in water (100 parts) at 200° in an open vessel or autoclave until the oxidising agent is expended. The product is dissolved in water and air blown in order to oxidise anthranols, and the alizarin is then precipitated by the addition of milk of lime. The precipitated salt is decomposed by hydrochloric acid, and the alizarin is separated from accompanying anthraquinone by solution in dilute aqueous sodium hydroxide and acidification of the filtered solution. Other processes have been suggested in which anthraquinone is heated with sodium or potassium hydroxides in the presence of sodium sulphite, with or without an oxidising agent such as sodium chlorate.

Purification of artificial alizarin. Commercial alizarin contains as impurities hydroxyanthraquinone, anthrapurpurin, flavopurpurin, and small quantities of other colouring matters.

In order to separate the alizarin from these, the crude commercial product is dissolved in dilute caustic soda, and the solution treated with carbonic acid until two-thirds of the colouring matter has been precipitated as acid sodium salt. The precipitate is collected, washed with water, decomposed with hydrochloric acid, the crude alizarin thus obtained dissolved in caustic soda, and the treatment with carbonic acid repeated twice more.

The purified product is then boiled with baryta water to remove hydroxyanthraquinone and anthraflavic acid (which dissolve), the barium salt of alizarin is collected, washed, decomposed by hydrochloric acid, and the alizarin either sublimed or recrystallised from alcohol.

Another method of separation is based on the temperatures at which the various constituents of the mixture sublime. Alizarin itself sublimes at 110°, flavopurpurin and anthrapurpurin at 160° and 170° respectively.

Alizarin crystallises from alcohol in red needles or prisms, which melt at 282°. With care alizarin can be sublimed in magnificent deep-red prisms, which, if the operation be performed on a large scale, may be obtained over an inch in length.

It dissolves in alkalis with a purple colour, and is completely precipitated from this solution by the addition of lime or baryta in the form of a blue precipitate of the calcium or barium salt. Heated with acetic anhydride to 160° alizarin forms a diacetyl compound $C_{14}H_6O_2(C_2H_3O)_2O_2$, which crystallises from alcohol in long yellow needles, melting at 160°. When treated with nitrous acid, alizarin yields anthraquinone. Nitric acid acts violently on alizarin with evolution of red vapours and formation of phthalic and oxalic acids. Distillation with zinc reduces alizarin to anthracene.

Alizarin is converted into purpurin by means of sulphuric acid at 225°. In Knecht and Hibbert's titanous chloride reduction method for the estimation of reducible substances it is found that one molecule of alizarin requires for reduction four atoms of hydrogen. On the other hand, Alizarin Orange (see below) is reduced to aminoalizarin under similar conditions.

When fused with alkaline hydroxides at a fairly high temperature, protocatechuic acid and benzoic acid are formed.

Salts of alizarin. *Calcium alizarate*

$$CaC_{14}H_6O_4,H_2O$$

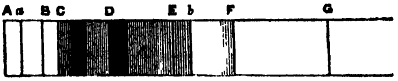
is precipitated by adding calcium chloride to an ammoniacal solution of alizarin as a purple mass. *Barium alizarate* $BaC_{14}H_6O_4,H_2O$ is prepared, like the calcium salt, by mixing an alkaline solution of alizarin with barium chloride. It is deep-violet when moist, almost black when dry, and very sparingly soluble in water. *Aluminium alizarate* $(C_{14}H_6O_4)_3Al_2O_6$(?) is obtained by precipitating an alkaline solution of alizarin with alum or aluminium hydroxide. It is a very fine red or rose-red precipitate. *Lead alizarate* $C_{14}H_6O_4Pb$ is obtained by mixing an alcoholic solution of alizarin with an alcoholic solution of sugar of lead.

Potassium hydrogen alizarate forms a compound with alizarin, brown-red crystals

$$C_{14}H_7O_4K ; C_{14}H_8O_4,$$

and a similar *tri*potassium *di*alizarate has been described. These substances are analogous to the quadroxalates.

Alizarin can readily be detected by means of the spectroscope, as it gives in alkaline solution two sharp absorption bands, one at D and one near G, as will readily be seen from the accompanying figure, which shows the absorption



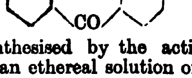
spectrum of a solution of alizarin in alcoholic potash.

Alizarin ferric acid $Fe(C_{14}H_6O_4)_3H_3$ yields well-crystallised sodium, ammonium, and potassium salts. The latter crystallises with $8H_2O$, and is obtained by the addition of alcoholic potassium hydroxide to a mixture of alcoholic solutions of alizarin and ferric acetate.

Literature.—Anderson (J. 1847–48, 749); Stenhouse (J. 1864, 543); Rochleder (Ber. 3, 295); Perkin (Chem. Soc. Trans. 23, 141); Graebe and Liebermann (Annalen Suppl. 7, 300; Ber. 3, 359); Baeyer and Caro (Ber. 7, 972); Liebermann (Annalen, 183, 206); Liebermann and Dehnst (Ber. 12, 1293); Schunck (Annalen, 66, 187); Wolff and Strecker (Annalen, 75, 8); Lagodzinski (Ber. 28, 1428); Widman (Ber. 9, 856); Liebermann and Hohenemser (Ber. 35, 1779); D. R. P. 116526; Perkin (Chem. Soc. Trans. 75. 453); Knecht and Hibbert (J. Soc. Dyers and Col., Dec. 1915); Weinland and Binder (Ber. 47, 977); Hofmann, Quoos and Schneider (Ber. 47, 1992); Heller (Zeitsch. Angew. Chem. 1906, 19, 669; Ber. 41, 361); Tyrer (Trans. 97, 1778); Hildebrand, Ellefson, and Beebe (J. Amer. Chem. Soc. 1917, 39, 2301).

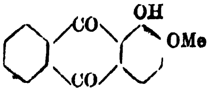
Other derivatives of alizarin. When treated with the ordinary re-agents, such as bromine, nitric acid, &c., alizarin forms a variety of valuable substitution products, some of which are used to a considerable extent as dyeing agents. The most important of these are the following:—

Alizarin α-methyl ether



may be synthesised by the action of diazomethane on an ethereal solution of monoacetylalizarin. Owing to the fact that monacetylalizarin is really a mixture of the two possible isomerides, the process results in a mixture of the two isomeric methyl ethers. Addition of alcoholic potassium hydroxide to the mixture precipitates the β-ether as potassium salt, the α-methyl ether remaining in the solution. The substance crystallises from aqueous methyl alcohol in slender orange-yellow needles melting at 178°–179°, and identical with a constituent of chay root (*q.v.*) (Oesch and Perkin, Proc. Chem. Soc. 1914, 30). The methoxy groups in aromatic compounds (except the nitrophenol ethers) are almost always resistant to alkaline hydrolysis, but this substance may be hydrolysed to alizarin by the prolonged action of boiling aqueous baryta. Acetylalizarin *a*-methyl ether occurs in yellow needles, melting at 212°.

Alizarin-β-methyl ether



The synthesis of this substance from hemipinic acid has already been described.

It can also be produced by treating the monopotassium salt of alizarin with methyl iodide or methyl sulphate.

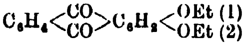
The substance crystallises from alcohol, and has the melting-point 224°–226°.

The dimethyl ether is not obtained by acting on the potassium salt of the monomethyl ether with methyl iodide.

The substance can, however, be obtained by reducing alizarin to desoxyalizarin and methylating the latter by means of methyl sulphate and sodium hydroxide in the usual manner. On oxidation of the resulting product with sodium chromate and acetic acid alizarin dimethyl ether is obtained in golden yellow needles. It is identical with a product obtained from 2-hydroxyanthraquinone by successive methylation, nitration, and treatment with methyl alcoholic sodium methoxide.

Oesch and Perkin (*l.c.*) have also obtained the substance by the methylation of alizarin *a*-methyl ether with methyl sulphate and potassium hydroxide.

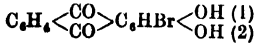
Alizarin diethyl ether



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_2{<}\begin{matrix}OEt\ (1)\\OEt\ (2)\end{matrix}$$

can be prepared by heating alizarin with potash and potassium ethyl sulphate at 160° (Habermann, Monatsh. 5, 228).

Monobromalizarin



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6HBr{<}\begin{matrix}OH\ (1)\\OH\ (2)\end{matrix}$$

This derivative can be prepared by heating alizarin with bromine and carbon disulphide to 180°–190° for four or five hours.

It is better prepared, however, by sulphonating alizarin with fuming sulphuric acid, and subsequently treating the solution with bromine.

It crystallises from glacial acetic acid in orange-coloured needles, which, when heated, first melt to an orange-coloured liquid and then sublime in orange-red needles.

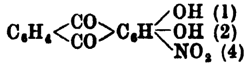
As a dyeing agent, monobromalizarin retains all the properties of combining with mordants possessed by alizarin, and the colours produced appear to be equally fast. The shade of colour produced is, however, not the same, the reds being less purple, and the purples less blue than those produced by alizarin.

Literature.—Perkin (Chem. Soc. Trans. 27, 401).

3 - Bromo - 1 : 2 - dihydroxyanthraquinone (D. R. PP. 77179, 78643) is obtained by the action of bromine on a solution of alizarin-3-sulphonic acid at 95°. It may or may not be identical with the above-described bromoalizarin. It forms brown-red needles, melting at 260°–261°, and yields a pale yellow diacetyl derivative, melting at 204°–205°. The solution of the substance in dilute sodium hydroxide is blue-violet.

3-Chloro-1 : 2-dihydroxyanthraquinone is similarly prepared and melts at 270°–271°. On benzoylation in pyridine solution a *dibenzoyl derivative*, melting at 184°, is obtained. On oxidation by means of sulphuric acid it yields 3-*chloro*-1 : 2 : 4-*trihydroxyanthraquinone* (chloropurpurin), melting at 242°–244°, and on nitration in acetic acid solution 3-*chloro*-4-*nitro*-1 : 2-*dihydroxyanthraquinone* is the product. The latter occurs in orange-yellow needles, which decompose at above 220°. The nitroxyl may be displaced by anilino on heating the substance with aniline, and the product crystallises in nearly black needles or plates melting at 223°-224° (Heller and Skraup, Ber. 46, 2703).

a-Nitroalizarin, Alizarin brown,



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H{<}\begin{matrix}OH\ (1)\\OH\ (2)\\NO_2\ (4)\end{matrix}$$

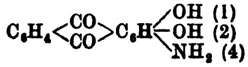
This substance is obtained by treating diacetyl or dibenzoyl alizarin with nitric acid.

It is manufactured by dissolving alizarin in fuming sulphuric acid and after cooling to −5° to −10°, treating with the calculated quantity of nitric acid dissolved in sulphuric acid.

a-Nitroalizarin crystallises from alcohol or glacial acetic acid in golden-yellow needles, melting at 194°–196°. It dissolves in caustic alkali with a blue-violet colour, but if only a minute quantity of alkali is employed the solution is of a fine crimson colour. The alkaline solution gives two absorption bands similar to alizarin. Nitroalizarin is easily reduced in alkaline solution with sodium amalgam or ammonium sulphide and amidoalizarin is the product.

On warming with sulphuric acid 1 : 2 : 3 : 4-tetrahydroxyanthraquinone is produced.

a-Aminoalizarin. Alizarin garnet, Alizarin cardinal



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H{<}\begin{matrix}OH\ (1)\\OH\ (2)\\NH_2\ (4)\end{matrix}$$

This valuable dye-stuff is obtained by the reduction of *a*-nitroalizarin. It crystallises from alcohol in small needles of a nearly black colour, but possessing a slight greenish metallic reflection.

Its alcoholic solution gives two absorption bands; the first is a little beyond D and the second near C. There is also a faint line close to F.

An excess of acetic anhydride at the boiling-point converts *a*-aminoalizarin into a *diacetyl derivative*, which crystallises in red-brown leaflets melting at 245°, whilst it appears that the moderated action of the reagent produces an isomeric diacetate crystallising in lustrous yellow needles. The *monobenzoyl derivative* is obtained by heating a suspension of the substance in nitrobenzene with benzoyl chloride. It occurs in brown needles, melting at 310°. Further action of benzoyl chloride produces the *dibenzoyl derivative*—light brown needles, melting at 255°. *a*-Aminoalizarin yields a sulphonic acid on treatment with fuming acid, and this may be changed into purpurin sulphonic acid by the action of nitrous acid. The diazonium derivatives obtained from α-aminoalizarin are relatively stable, and on strongly heating purpurin is obtained as a sublimate. Alizarin-α-diazochloride does not couple with known intermediates with formation of azo- compounds.

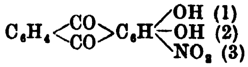
Dyeing Properties of α-Nitro- and α-Aminoalizarin. These colouring matters possess the power of dyeing ordinary madder mordants. α-Nitroalizarin gives with alumina mordants very clear orange-red colours, not unlike some of the colours produced with aurin, and with iron mordants reddish-purple colours. Aminoalizarin gives with alumina mordants purple colours, and with iron a bluish or steel-like colour.

It is used for wool-dyeing and calico-printing.

Alizarin Maroon is a mixture of aminoalizarins and purpurins obtained by the reduction of the product of nitration of commercial alizarin in sulphuric acid solution. On alumina mordants it produces a garnet red, maroon on chrome.

Literature.—Perkin (Chem. Soc. Trans. 30, 578); Brasch (Ber. 24, 1610); Schunck and Römer (Ber. 12, 587); D. R. PP. 66811, 74431, 74598; Schultz and Erber (J. pr. Chem. 74, 275).

β-Nitroalizarin, Alizarin Orange



$$\mathrm{C_6H_4}<\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}>\mathrm{C_6H}<\begin{matrix}\mathrm{OH}\ (1)\\ \mathrm{OH}\ (2)\\ \mathrm{NO_2}\ (3)\end{matrix}$$

β-Nitroalizarin is prepared by the action of nitric acid on alizarin and also by boiling dinitro-2-hydroxyanthraquinone with caustic soda of 20 p.c.

It is manufactured in large quantities by the action of nitric acid on alizarin dissolved in sulphuric acid containing boric acid. The influence of the boric acid on the position attacked by the nitric acid is probably due to the formation of a boric ester of alizarin.

The crude β-nitroalizarin is purified by crystallisation from glacial acetic acid.

β-Nitroalizarin crystallises in orange-yellow needles which melt with decomposition at 244°. When carefully heated it sublimes, with a good deal of decomposition, in yellow needles. Dissolved in alkalis it forms a purple solution; the *sodium* salt is insoluble in an excess of caustic soda. The *calcium* salt is an insoluble violet-red precipitate, which is not decomposed by carbonic acid (distinction from alizarin). Treated with glycerol and sulphuric acid, β-nitroalizarin is converted into alizarin blue.

The diacetate of β-nitroalizarin crystallises in yellow needles melting at 218°.

β-Nitroalizarin is prepared on the large scale, and comes into the market under the name of 'Alizarin orange.' In dyeing it is applied to the various fibres in the same way as alizarin; but although it yields fast colours, it has as yet found only comparatively limited employment. Applied to wool, it gives the following shades:—

With an aluminium mordant it yields a very good orange; with stannous chloride mordant, a reddish or yellowish orange, according to the amount of mordant used; with copper sulphate mordant, a good reddish-brown is obtained; with ferrous sulphate, a purplish-brown; and with bichromate of potash, a dull brownish-red. The dye may also be applied to unmordanted wool in a bath containing acetic or oxalic acids.

Literature.—Rosenstiehl (Bull. Soc. chim. 26, 63); Schunck and Römer (Ber. 12, 584); Simon (Ber. 15, 692); Bayer & Co. D. R. P. 74562; Barnes (J. Soc. Dyers & Col. 15, [1] 11).

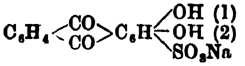
β-Aminoalizarin is changed by benzoyl chloride into a *dibenzoyl derivative*, yellow needles melting at 252°, and this may be hydrolysed by sulphuric acid to a *monobenzoate* melting at 275°. In contradistinction from the corresponding α-derivative, alizarin-β-diazochloride couples with R-salt in alkaline solution, but the product has feeble tinctorial power.

Alizarin Imide. This derivative of alizarin is obtained by heating the substance with ammonia under pressure (Bayer), and also by reducing freshly precipitated alizarin in ammoniacal suspension with zinc dust followed by air oxidation of the resulting solution. According to Prud'homme, alizarin and other hydroxyanthraquinones may be converted into condensation products with ammonia by heating in glycerol with ammonium carbonate. Scholl and Partheg prepare the substance by heating alizarin with aqueous ammonia at 140°. It may be crystallised from pyridine and decomposes with evolution of ammonia at 250°. It is regarded as 1-*hydroxy*-2-*aminoanthraquinone imide*.

Literature.—Prud'homme (Bull. Soc. chim. [iii.] 35, 71; *ibid.* 666); Scholl and Partheg (Ber. 39, 1201).

Leucoalizarin, 1 : 2-Dihydroxyanthranol. This substance is easily prepared by warming alizarin with a dilute alkaline solution of sodium hydrosulphite. It crystallises from acetic acid in brown leaflets melting at 150°, and is easily reoxidised into alizarin (Grandmougin, Rev. Gen. Nat. Col. 21, 44).

Alizarin Red S, Alizarin Powder W (By.), **Alizarin Red WS** (M. L. B.)



$$\mathrm{C_6H_4}<\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}>\mathrm{C_6H}<\begin{matrix}\mathrm{OH}\ (1)\\ \mathrm{OH}\ (2)\\ \mathrm{SO_3Na}\end{matrix}$$

This dyestuff is the sodium salt of the monosulphonic acid of alizarin. It is easily prepared by the action of concentrated sulphuric acid on alizarin.

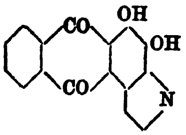
It yields brilliant scarlet red shades with an aluminium mordant, bordeaux red with chromium.

Like many alizarin derivatives, this substance is an indicator. It is more sensitive than methyl orange, the colour change occurring between $\mathrm{P\overset{+}{H}}=3{\cdot}7$ (yellow) and $\mathrm{P\overset{+}{H}}=4{\cdot}2$ (pink).

Literature.—Graebe and Liebermann (Annalen, 160, 144); Walpole (J. Soc. Chem. Ind. 1915, 153).

1 : 2-Dihydroxyanthraquinone-3 : 5-disulphonic acid is obtained, together with quinizarin-α-sulphonic acid, when anthraquinone-1-sulphonic acid or its potassium salt is heated with fuming sulphuric acid (40 p.c. SO_3) and boric acid at 130°–135°. The alizarin derivative is separated by taking advantage of its more sparing solubility. On heating with 70 p.c. sulphuric acid the disulphonic acid is changed into an isomeride of Alizarin Red S, namely 1 : 2-dihydroxyanthraquinone-5-sulphonic acid.

Alizarin Blue,



This important colouring matter, discovered by Prud'homme, is obtained by treating β-nitroalizarin with glycerol and sulphuric acid or by treating β-amino alizarin with glycerol, nitrobenzene, and sulphuric acid. Its chemical constitution was first demonstrated by Graebe, who showed that this substance was related to alizarin in precisely the same way as quinoline is to benzene, *i.e.* that alizarin blue is a quinoline of alizarin.

Preparation.—1 part of β-nitroalizarin, 5 parts sulphuric acid, and 1½ glycerol (of sp.gr. 1·262) are mixed and gently heated.

At 107° the reaction commences and soon becomes very violent, the temperature rising to 200°. After the frothing has subsided, the mass is poured into water, the product well boiled, filtered, and the residue extracted three or four times with very dilute sulphuric acid. The combined extracts on cooling deposit the crude alizarin blue sulphate in brown crystals. These are collected, washed with water till neutral, mixed with water, and borax added until the solution becomes brownish-violet. The precipitate thus formed is filtered off, washed with water, and decomposed with a dilute acid, the crude alizarin blue thus obtained being purified by recrystallisation from benzene or glacial acetic acid.

A more recent method of preparation, also due to Prud'homme, consists in heating formyl-β-aminoalizarin with glycerol and sulphuric acid at 100°.

Alizarin blue crystallises from benzene in brownish-violet needles which melt at 270°, and at a higher temperature give off orange-red vapours which condense in the form of blue needles.

It is insoluble in water, sparingly soluble in alcohol and ether, more readily soluble in hot benzene. It dissolves in ammonia, potash, or soda, forming blue solutions which become green when mixed with an excess of alkali.

Alizarin blue combines with both bases and acids.

The barium salt $BaC_{17}H_7NO_4BaO+\frac{1}{2}H_2O$ is a greenish-blue precipitate. The following salts of alizarin blue with acids have been prepared:—

$C_{17}H_9NO_4,HCl$ is a red crystalline precipitate formed by passing dry hydrochloric acid gas through a solution of alizarin blue in boiling benzene. When treated with water it is completely decomposed into its constituents. The sulphate crystallises in red needles. The acetate $C_{17}H_9NO_4.C_2H_4O_2$ crystallises in blue plates.

Alizarin blue also combines with picric acid forming a compound $C_{17}H_9NO_4{\cdot}C_6H_2(NO_2)_3O$, which crystallises from benzene in long orange-red prisms melting at 245°. This compound is completely decomposed by water. One of the most important compounds of alizarin blue is the sodium bisulphite compound

$$C_{17}H_9NO_4{\cdot}2NaHSO_3$$

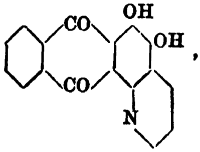
This product is manufactured on a large scale and sold under the name of 'Alizarin Blue S.' It dissolves readily in water, with a brownish-red colour. Alizarin blue is met with in commerce in two forms, viz. as a paste containing about 10 p.c. of dry substance, and as a powder. The former is nearly insoluble in water, while the latter, which is the bisulphite compound (described above), dissolves readily. This soluble kind is now almost entirely used in dyeing. In dyeing cotton with alizarin blue a chromium mordant is used, but in the case of wool, bichromate of potash gives the best results.

Alizarin blue with an alumina or iron mordant is also used for dyeing silk.

Alizarin blue is used largely as a substitute for indigo in calico-printing works. It is one of the most stable colouring matters, and is even said to be faster than indigo itself.

Literature.—Prud'homme (Bull. Soc. chim. 28, 62); Graebe (Annalen, 201, 333); Auerbach (Chem. Soc. Trans. 35, 800); Prud'homme and Rabaut (Bull. Soc. Ind. Mulhouse, 1893, 223).

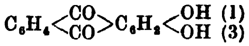
Alizarin Green S (M)



, $NaHSO_3$.

This dyestuff is prepared from α-aminoalizarin by treatment with glycerol, nitrobenzene, and sulphuric acid, and it may also be produced from formyl-α-aminoalizarin by the action of glycerol and sulphuric acid at 100°. Its production and properties resemble those of alizarin blue. It is employed in printing, and is used with a nickel magnesia mordant.

Purpuroxanthin. 1 : 3-Dihydroxyanthraquinone



$$C_6H_4{<}^{CO}_{CO}{>}C_6H_2{<}^{OH\ (1)}_{OH\ (3)}$$

Purpuroxanthin exists in small quantities in madder. It can be prepared by heating purpurin $C_{14}H_5(OH)_3O_2$ with iodide of phosphorus and water, or more readily by boiling purpurin with caustic soda and chloride of tin.

Preparation. — Purpurin is dissolved in a boiling solution of caustic soda (10 p.c.), and chloride of tin added until the solution loses its deep-red tint and becomes of a yellow colour. Hydrochloric acid is then added, the precipitate washed with strong hydrochloric acid, dissolved in baryta water, reprecipitated with hydrochloric acid and crystallised from alcohol.

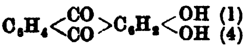
Purpurin is also readily reduced by means of an alkaline solution of sodium hydrosulphite.

Purpuroxanthin crystallises in reddish-yellow needles which melt at 262°–263°. It dissolves in alkalis with a reddish colour. If the solution in caustic potash be boiled in the air, it absorbs oxygen, the purpuroxanthin being reconverted into purpurin.

It is not a mordant dyestuff.

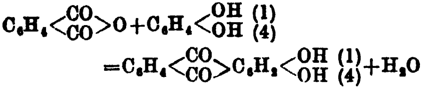
Literature.—Schützenberger and Schiffert (Bull. Soc. chim. 4, 12); Liebermann (Annalen, 183, 213); Schunck and Römer (Ber. 10, 172).

Quinizarin. 1 : 4-Dihydroxyanthraquinone



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2<\begin{matrix}OH\ (1)\\OH\ (4)\end{matrix},$$

is obtained by heating a mixture of quinol or *p*-chlorphenol and phthalic anhydride with sulphuric acid.



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O+C_6H_4<\begin{matrix}OH\ (1)\\OH\ (4)\end{matrix}$$
$$=C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2<\begin{matrix}OH\ (1)\\OH\ (4)\end{matrix}+H_2O$$

Together with alizarin and purpurin, it is obtained by the action of ammonium persulphate on anthraquinone in sulphuric acid solution; also on heating anthraquinone in sulphuric acid, containing boric acid, with nitrous fumes.

Preparation.—Equal parts of *p*-chlorphenol and phthalic anhydride are heated to 200°–210° for some hours, with ten times as much sulphuric acid as chlorphenol used. The product is poured into two or three times its volume of water, and after standing for twenty-four hours, the precipitate is filtered off, washed and pressed.

The crude product is then boiled with water to free it from phthalic acid, dissolved in caustic soda, precipitated with hydrochloric acid and recrystallised from alcohol. In order to remove a small quantity of purpurin, which is nearly always present, the crude quinizarin is then washed with cold dilute caustic soda as long as the solution is coloured red, and the residue recrystallised from toluene.

Quinizarin is also obtained by heating either the 1- or the 2-hydroxyanthraquinones with nitrites and boric acid in sulphuric acid solution at 180°–200°. The formation of quinizarin from 2-hydroxyanthraquinone is certainly remarkable, but the expected product, namely purpurin, is formed in traces only. A process of theoretical interest is that of Dienel (Ber. 1906, 39, 926), who converts α-anthrol by means of a hot aqueous alcoholic solution of sodium nitrite and zinc chloride into two isomeric nitroso-derivatives which may be reduced to amino compounds and oxidised to 1 : 2- and 1 : 4-anthraquinones respectively. The latter crystallises from alcohol in long yellow needles which melt at 206° (*cf.*, however, Haslinger, Ber. 39, 3537, who gives 190°) and by successive reduction, acetylation, oxidation, and hydrolysis may be changed to quinizarin.

Quinizarin crystallises from alcohol in red needles which melt at 192°–193°, and sublime at a high temperature with partial decomposition. It dissolves readily in benzene. The solutions in ether and sulphuric acid are characterised by a beautiful greenish-yellow fluorescence. Quinizarin dissolves in baryta, forming a blue solution from which it is reprecipitated on passing carbonic acid (distinction from alizarin).

The tinctorial effects produced by quinizarin on fabrics mordanted with iron, chromium, or aluminium are about one-tenth of those produced by an equal amount of alizarin.

When fused with potash it is converted into hydroxychrysazin $C_{14}H_8O_5$. Quinizarin forms a diacetate which melts at 200°.

Literature.—Baeyer and Caro (Ber. 8, 152); Schunck and Römer (Ber. 10, 554); Bayer & Co. D. R. P. 81245 (*see* also above).

Leucoquinizarin is obtained by the reduction of quinizarin with sodium hydrosulphite and sodium hydroxide. It is a yellow crystalline substance melting at 135°, and is of importance since it condenses with aromatic amines more readily than quinizarin itself, and is thus employed in the manufacture of some of the important acid dyes of this group.

2-Nitroquinizarin is the product obtained by the nitration of quinizarin in acetic acid or nitrobenzene solution. It forms brick-red crystals which dissolve in sulphuric acid to a cerise solution and dyes wool brown on an alumina mordant, violet-brown on chromed wool.

Quinizarin sulphonic acid is obtained by the action of sodium sulphite on a hot aqueous suspension of quinizarin, preferably in the presence of an oxidising agent such as pyrolusite.

Fuming sulphuric acid (70–80 p.c. SO_3) in large excess converts quinizarin at 20°–40° into 1 : 2 : 5 : 8-tetrahydroxyanthraquinone (Schmidt Bull. Soc. chim. 1914, (15) 12, 1).

The hydrogen atoms in quinizarin are not readily displaced by halogens, but, on the other hand, an additive product, a *hexabromide* is formed at 0°. At 40° the product is *bromoquinizarin dibromide*, and even at temperatures between 100° and 230° only a *dibromoderivative* is produced.

Dichloroquinizarines. 3 : 6-, 3 : 4-, and 4 : 5-Dichlorophthalic anhydrides react with quinol in presence of boric acid to produce dichlorodihydroxybenzoyl benzoic acids which are changed by sulphuric acid into corresponding dichloroquinizarines.

5 : 8-**Dichloroquinizarin** crystallises in brown-red needles melting at 266°, and forms an *acetyl derivative* melting at 170°. When its potassium salt is heated with potassium phenoxide during eight hours at 180° it is changed to 8-*chloro-5-phenoxyquinizarin*, light red needles melting at 243°. The phenoxy derivative is transformed by *p*-toluidine at 150° in presence of potassium and copper acetates into 8-*p-toluidino-5-phenoxyquinizarin* (m.p. 278°). 5 : 8-Dichloroquinizarin reacts similarly with aniline forming 5 : 8-*dianilinoquinizarin* melting at 245°.

5 : 6-**Dichloroquinizarin** melts at 208°, and its *acetyl derivative* at 140°.

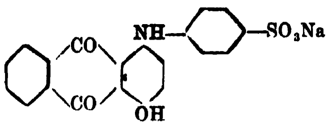
6 : 7-**Dichloroquinizarin** melts at 288° and forms an *acetate* melting at 125°.

Literature.—M. Frey (Ber. 45, 1358).

Acid dyes derived from quinizarin or its derivatives. Quite a considerable sub-group of anthracene dyes have been obtained by acting on quinizarin or its derivatives with amines usually in presence of boric acid. One or two of the hydroxyls of quinizarin may be replaced by arylamino groups, or if desired, one of the groups introduced may be amino or alkylamino. The products are sulphonated and are then acid wool dyes. The firm of Cassella occasionally condense leucoquinizarin with ready formed toluidine sulphonic acid in presence of boric acid. Friedländer and Schick (Zeitsch. Farben u. Textil Chemie, 1902, 2, 429; 1903, 3, 218) have shown that the reaction leading to the formation of these dyes is reversible in the case of the condensation with leucoquinizarin, and have applied this observation in order to hydrolyse some dyes found in commerce and so prove their nature. They find that acid dyes of this series which contain a sulphonated anilino- or toluidino- group will usually yield leucoquinizarin or similar substance, together with an aniline or toluidine sulphonic acid by boiling with stannous chloride in aqueous alcoholic hydrochloric acid solution.

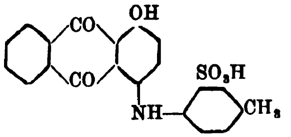
Alizarin Emeraldol G, Alizarin Uranole R, Alizarin Geranol B, Alizarin Heliotrope R, BB, and Alizarin Marine Blue RG, W, are examples of acid dyes of similar type to those described, but of undisclosed constitution.

Quinizarin Blue



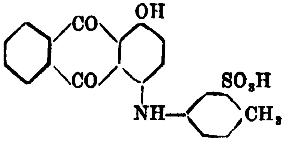
This dyestuff is prepared by heating quinizarin and aniline in molecular proportions and sulphonating the product. From an acid bath it dyes wool a red shade of blue, and gives a greenish-blue with chromed wool.

Alizarin Irisol D (R) (Bayer, D. R. PP 86150 and 91149).



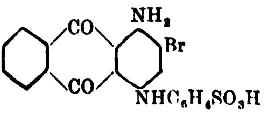
Quinizarin or leucoquinizarin is condensed with *p*-toluidine and the product sulphonated. The substance is isomeric with Alizarin Cyanol Violet (*q.v.*).

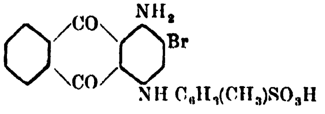
Alizarin Cyanol Violet R (Cassella, D. R. PP. 172464 and 181879).



Leucoquinizarin is condensed with 4-aminotoluene-2-sulphonic acid and the product oxidised.

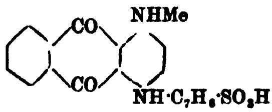
Alizarin Pure Blue and **Alizarin Blue GG** have the respective formulæ :—





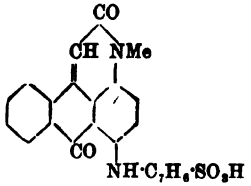
Alizarin Cyanol B (Cassella, D. R. PP. 183395, 114262, 119362). The mixture of 1 : 5- and 1 : 8-anthraquinone disulphonic acids is changed by ammonia and sodium chlorate at 170° to corresponding diamino anthraquinones amd aminoanthraquinonesulphonic acids. The latter are brominated to mixed dibromo-derivatives, and these are condensed with aniline and sulphonated.

Alizarin Astrol



dyes wool greenish-blue from an acid bath.

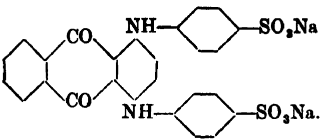
Alizarin Rubinol G, 3G, GW (Bayer, D. R. P. 201904)



is obtained by the sulphonation of *p*-toluidino-N-methylanthrapyridone. It dyes wool in red shades from an acid-bath.

Quinizarin Green.

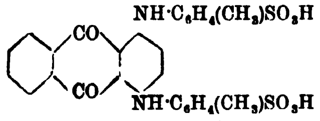
Quinizarin is treated with an excess of aniline and the product sulphonated. The dyestuff is the sodium salt of the sulphonic acid, and has the constitution



The green shades produced on wool from an acid-bath are fast to light and milling.

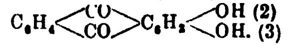
Anthraquinone Green is the corresponding monosulphonic acid.

Alizarin Cyanine Green E, G Extra, K (Bayer)



This dye is obtained by sulphonating the product of the complete tolylation of quinizarin. It dyes wool from an acid bath a very vivid green. This dye has now displaced for most purposes the Alizarin Viridine which is similarly prepared from Alizarin Bordeaux. An isomeride with very similar properties is *Alizarin Brilliant Green G, SE* (*Cassella*), and the difference in constitution is the same as that between Alizarin Irisol and Alizarin Cyanol Violet. The dye now in question is obtained by carrying to the second stage the condensation between leucoquinizarin and 4-aminotoluene-2-sulphonic acid.

Hystazarin. 2 : 3-Dihydroxyanthraquinone,



$$C_6H_4\begin{matrix}<CO>\\<CO>\end{matrix}C_6H_2\begin{matrix}<OH\ (2)\\<OH.\ (3)\end{matrix}$$

This substance is formed, together with alizarin, when a mixture of pyrocatechol and phthalic anhydride is treated with sulphuric acid—5 grams of pyrocatechol, 6·8 grams phthalic anhydride and 75 grams sulphuric acid are heated for 4½ to 5 hours to 340–150° on a sand-bath.

The resulting product, while still warm, is poured into ¾ litre of water, heated to boiling, and filtered hot.

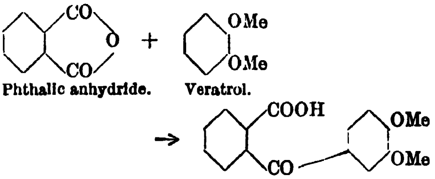
The dark-green precipitate thus obtained is well washed with hot water, dissolved in dilute potash, and the dark-blue solution precipitated by dilute sulphuric acid. The precipitate is washed with water, dried on a porous plate, and treated with boiling alcohol in an extraction apparatus, by which means a considerable portion is dissolved.

The dark-red solution on evaporation yields an orange-red mass, which consists of alizarin and hystazarin. These two substances are readily separated by treatment with boiling benzene, which dissolves the alizarin and leaves the hystazarin; the latter may then be further purified by recrystallisation from acetone.

Yield 1½ p.c. alizarin and 12 p.c. hystazarin of pyrocatechol used.

The following conditions for the preparation have also been published: 30 grams pyrocatechol are heated with 42 grams phthalic anhydride and 300 grams sulphuric acid at 180°–200° for half an hour. Yield of hystazarin was 6 grams, and of alizarin 1 gram.

Hystazarin may be synthesised by the following series of reactions:—Phthalic anhydride condenses with veratrol in carbon disulphide solution under the influence of aluminium chloride.


Phthalic anhydride.

Veratrol.

3 : 4 : dimethoxybenzoylbenzoic acid.

The 3 : 4-dimethoxybenzoylbenzoic acid thus produced yields 2 : 3 : dimethoxyanthraquinone on heating with concentrated sulphuric acid. This is hystazarindimethyl ether and yields hystazarin on demethylation.

Hystazarin crystallises from acetone in orange-yellow needles, which do not melt at 260°.

It is almost insoluble in benzene, difficultly soluble in xylene, soluble in hot alcohol, ether, glacial acetic acid, and acetone.

It dissolves in alkalis with a blue (cornflower) colour, in ammonia with a violet colour, and in concentrated sulphuric acid with a blood-red colour. The barium salt is a blue precipitate, the calcium salt a violet precipitate; both are insoluble in water.

Hystazarin possesses only very feeble tinctorial properties. The faint red colour produced with an aluminium mordant differs in shade from the alizarin red. The solution of hystazarin in dilute sodium hydrate absorbs the yellowish red and violet rays of the spectrum. A very dilute solution shows two lines in the yellow, $\lambda=619{\cdot}8$, $\lambda_1=587{\cdot}4$. Distilled over zinc-dust, hystazarin yields relatively large quantities of anthracene.

Hystazarin is changed by sulphuric acid at 200° slowly into alizarin. It is probable that the reaction is one of hydrolysis into phthalic acid and catechol and subsequent condensation in the ortho- position to the hydroxyl group.

Literature. — Liebermann and Schoeller (Ber. 21, 2501–2508); Lagodzinski and Lorétan (Ber. 28, 118); Liebermann and Hohenemser (Ber. 35, 1778); Schrubsdorf (Ber. 36, 2936).

Diacetyl hystazarin $C_{14}H_6O_2(OC_2H_3O)_2$ crystallises from acetic acid in needles, which melt at 205°–207°.

2 : 3-*di*-**Hydroxyanthranol** is obtained by the reduction of hystazarin with zinc dust and ammonia. It occurs in yellow-brown needles melting at 282°, and forms a *triacetyl derivative* melting at 163°.

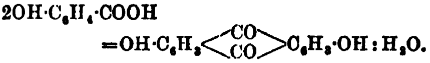
1-Nitrohystazarin is obtained when hystazarin is nitrated in sulphuric acid solution by means of a molecular proportion of nitric acid. Further nitration leads to 1 : 4-*dinitrohystazarin*, and both these derivatives have only a slight tinctorial power on mordants.

1 : 4-Dibromohystazarin is obtained by brominating the substance at 150° in a sealed tube. It melts at 127°–129° and dissolves in alkaline solutions with a violet colour.

Anthraflavic acid. 2 : 6-Dihydroxyanthraquinone

$$(6)\ HO{\cdot}C_6H_3{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_3{\cdot}OH.\ (2)$$

Anthraflavic acid is prepared by fusing α-anthraquinone disulphonic acid with potash, and is therefore nearly always present in artificial alizarin. Synthetically it has been obtained by heating *m*-hydroxybenzoic acid with sulphuric acid to 190°.


$$2OH{\cdot}C_6H_4{\cdot}COOH = OH{\cdot}C_6H_3{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_3{\cdot}OH : H_2O.$$

This mode of formation proves that this substance contains the two hydroxyl groups in different benzene rings.

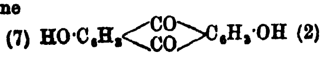
Anthraflavic acid crystallises from alcohol in yellow needles which melt above 330°. The pure substance when carefully heated sublimes partially in yellow needles, leaving a considerable quantity of a carbonaceous residue. Anthraflavic acid does not dye mordanted cloth. It dissolves in alkalis forming a yellowish-red solution, and in sulphuric acid forming a green solution, the absorption spectrum of which shows a broad band between the blue and the green. Anthraflavic acid forms a number of salts, of which the sodium salt is the most characteristic. This salt is sparingly soluble in water, and is remarkable for the ease with which it crystallises; this distinguishes it from *iso*anthraflavic acid, and gives a ready means of separating these two substances. When treated with acetic anhydride, anthraflavic acid forms a diacetate melting at 228°–229°.

Literature.—Perkin (Chem. Soc. Trans. 1871, 24, 1109; 26, 19); Schunck and Römer (Ber. 9, 379; 11, 970); Liebermann (Ber. 5, 968); Rosenstiehl (Bull. Soc. chim. 29, 401–434); Barth and Senhofer (Ber. 170, 100).

Tetranitroanthraflavic acid consists of yellow needles exploding without fusion at 307°. It is obtained by the action of nitric acid on anthraflavic acid. By the employment of the calculated amount of nitric acid it is possible to obtain a *dinitro derivative* which dyes wool from an acid-bath.

Literature.—Schradinger (Ber. 8, 1487).

*Iso***Anthraflavic acid.** 2 : 7-Dihydroxyanthraquinone



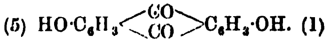
$$\text{(7) } HO\cdot C_6H_3{<}\substack{CO\\ CO}{>}C_6H_3\cdot OH \text{ (2)}$$

is formed when β-anthraquinone disulphonic acid is fused with potash, and is therefore always contained in crude alizarin. In preparing it, crude alizarin is dissolved in dilute caustic soda, the solution precipitated with hydrochloric acid, and the precipitate dissolved in cold baryta water and filtered. (In this way *iso*anthraflavic acid, which forms a soluble baryta compound, is easily separated from alizarin, anthrapurpurin, and anthraflavic acid, which yield insoluble barium compounds.) The filtrate is treated with hydrochloric acid, and the precipitate recrystallised from alcohol. *Iso*anthraflavic acid crystallises in long yellow needles, containing 1 mol. H_2O, which can be driven off at 150°. It melts above 330° and sublimes at a high temperature in lustrous yellow needles. It dissolves easily in alkalis forming a deep-red solution, but it does not dye mordanted cloth. Fused with potash *iso*anthraflavic acid yields anthrapurpurin.

The diacetate of *iso*anthraflavic acid melts at 195°.

Literature.—Schunck and Römer (Ber. 9 379).

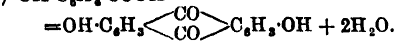
Anthrarufin. 1 : 5-Dihydroxyanthraquinone



$$\text{(5) } HO\cdot C_6H_3{<}\substack{CO\\ CO}{>}C_6H_3\cdot OH. \text{ (1)}$$

Anthrarufin is formed together with anthraflavic acid and metabenzdioxyanthraquinone by heating *m*-oxybenzoic acid with sulphuric acid.

(2) $OH\cdot C_6H_4\cdot COOH$



$$=OH\cdot C_6H_3{<}\substack{CO\\ CO}{>}C_6H_3\cdot OH + 2H_2O.$$

It may also be obtained by fusing *o*-anthraquinone disulphonic acid with potash.

Another process depends on the fact that it is the chief product when anthraquinone is oxidised with sulphur trioxide under the following conditions :—Anthraquinone (50 parts) is heated with fuming sulphuric acid (1000 parts containing 80 p.c. SO_3) and boric acid (20 parts) for 36 hours at 100° under pressure.

Anthrarufin is manufactured, mainly as an intermediate for alizarin saphirol, by heating anthraquinone-1 : 5-disulphonic acid with milk of lime under pressure.

Anthrarufin crystallises in yellow needles which melt at 280° and sublime easily at a higher temperature (distinction from anthraflavic acid). It dissolves with difficulty in ammonia and soda, but more readily in potash.

Anthrarufin dissolves in sulphuric acid, forming a deep-red solution, the colour of which is so intense that it is still easily apparent in solutions containing only 1 part in 10,000,000.

Anthrarufin forms a diacetate which melts at 244°-245°.

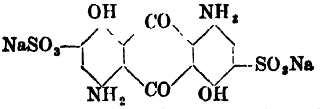
Anthrarufin dimethyl ether is obtained on boiling 1 : 5 : dinitroanthraquinone with methyl alcoholic caustic soda. The substance forms deep-red needles of m.p. 230°.

Literature.—Schunck and Römer (Ber. 11, 1175) ; Liebermann and Dehnst (Ber. 12, 1289) ; Bayer and Co. D. R. P. 101220 ; Pleus (Ber. 35, 2923).

Anthrarufin monoethyl ether occurs in yellow needles melting at 164° and yielding an *acetyl derivative* melting at 173°.

Anthrarufin diethyl ether forms long silky needles melting at 178°.

Alizarin Saphirol B. *Alizarin Delphinol.*

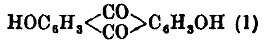


is an important blue acid wool-dye derived from anthrarufin by successive sulphonation, nitration, and reduction. This dyestuff excels in respect to its fastness to light.

It may also be obtained by the reduction of 1 : 5-dinitroanthraquinone in alkaline solution followed by acidification and sulphonation. The first product is a dihydroxylaminoanthraquinone, and this rearranges into an amino-compound by the action of the acid. Dinitroanthrarufin may also form the source of this or a very similar dyestuff into which it is converted by the action of sulphites. *Alizarin Saphirol SE* is the monosulphonic acid. There are also dyestuffs of this type which contain a bromine atom in the anthraquinone nucleus.

Alizarin Celestol is obtained by the action of formaldehyde on Alizarin Saphirol.

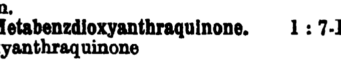
1 : 6-**Dihydroxyanthraquinone**



$$\text{(6) } HOC_6H_3{<}\substack{CO\\ CO}{>}C_6H_3OH \text{ (1)}$$

This was the last of the dihydroxyanthraquinones to be obtained, it having been prepared by Frobenius and Hepp in 1907 (Ber. 40, 1048). 1-Nitroanthraquinone-6-sulphonic acid was converted by sodium methoxide into 1-methoxyanthraquinone-6-sulphonic acid, and the latter hydrolysed to a hydroxyanthraquinone sulphonic acid by heating with sulphuric acid. The sodium salt was then prepared and heated with milk of lime at 195° under pressure. The substance crystallises in orange-yellow needles melting at 271°-272°, and dissolving in ammonia or potassium hydroxide to a yellow solution. Oxidation by heating under pressure with a solution of sodium hydroxide and sodium nitrate results in the production of flavopurpurin.

Metabenzdioxyanthraquinone. 1 : 7-Dihydroxyanthraquinone



$$\text{(7) } HO—C_6H_3{<}\substack{CO\\ CO}{>}C_6H_3—OH \text{ (1)}$$

Literature.—Schunck and Römer (Ber. 11, 1176) ; Liebermann and Dehnst (Ber. 12, 1289).

Metabenzdihydroxyanthraquinone $C_{14}H_8O_4$ is formed together with anthraflavic acid and anthrarufin by heating *m*-hydroxybenzoic acid with sulphuric acid (*v. supra*). It is separated from these by treatment with benzene and subsequent recrystallisation from dilute alcohol. Metabenzdihydroxyanthraquinone forms yellowish needles which melt at 291°-293°, and sublime at a higher temperature almost without decomposition. It dissolves in alkalis with a dark-yellow colour, and in concentrated sulphuric acid, forming a brownish-yellow solution, which shows no absorption bands.

The diacetate of metabenzdihydroxyanthraquinone melts at 199°.

Literature.—Schunck and Römer (Ber. 10, 1225); Rosenstiehl (Ber. 9, 946).

Chrysazin. 1 : 8-Dihydroxyanthraquinone is formed by fusing χ-anthraquinonedisulphonic acid with potash, or by treating hydrochrysamid $C_{14}H_2(NH_2)_4(OH)_2O_2$ with nitrous acid and alcohol. (N.B.—Hydrochrysamid is obtained by the reduction of chrysammic acid $C_{14}H_4(NO_2)_4O_4$, which is the product of the action of nitric acid on aloes.)

It is manufactured by heating anthraquinone-1 : 8-disulphonic acid with milk of lime under pressure with or without the addition of calcium chloride.

Chrysazin forms reddish-brown needles, which melt at 191°. It dissolves in alkalis and sulphuric acid, with a red colour. Its diacetate melts at 227°–232°.

Crude dinitroanthraquinone contains a compound which is converted into chrysazin dimethyl ether on treatment with methyl alcoholic potash.

Literature.—Liebermann (Annalen, 183, 184).

Derivatives of Chrysazin.

Monopotassium salt. Chrysazin is dissolved in a little hot dilute potassium hydroxide solution. The salt separates in orange-red needles which contain water of crystallisation, and on heating at 100° becomes anhydrous, the colour changing to violet.

Chrysanthranol, 1 : 8 - Dihydroxyanthranol. This substance, which possesses therapeutic value similar to that which characterises chrysarobin, may be obtained by the reduction of chrysazin with hydriodic acid and phosphorus. It melts at 177°, and forms a triacetyl derivative melting at 210°.

4 : 5-Dichlorochrysazin is obtained by passing chlorine into a suspension of chrysazin in sulphuric acid of such a concentration that the b.p. is 120°.

Chrysazinamide, 1-Amino-8-hydroxyanthraquinone is obtained by saturating a chrysazin paste with ammonia at 0° and heating in a sealed tube.

Chrysazin-disulphonic acid is obtained by sulphonation of chrysazin with oleum (20 p.c. SO_3). It is isolated as a potassium salt, and on fusion with alkali yields a dihydroxychrysazin melting at 292° (acetyl derivative, m.p. 233°–240°) and isomeric, but not identical with a tetrahydroxyanthraquinone obtained by fusing chrysazin with potassium hydroxide in a vacuum. The latter substance occurs in dark red needles melting at 217°, and forming a tetracetyl derivative melting at 195°.

Dinitrochrysazin (probably 4 : 5-dinitro-1 : 8-dihydroxyanthraquinone). Chrysazin dimethyl ether (obtained from 1 : 8-dinitroanthraquinone by the action of sodium methoxide) is nitrated by means of a mixture of nitric and sulphuric acids. The resulting *dinitrochrysazin dimethyl ether* crystallises from chlorobenzene in green needles melting at 232°–233°. It may be hydrolysed by hot 10 p.c. sulphuric acid, and the dinitrochrysazin separates from chlorobenzene in orange-yellow crystals melting at 232°–234°. Chrysazin is coming more and more into use as an intermediate for the preparation of dyestuffs, and, for example, the processes which are used to convert anthrarufin into Alizarin Saphirol may also be applied to chrysazin, and the product is a valuable wool dye. For this reason it is not the invariable practice to separate anthraquinone-1 : 5- and 1 : 8-disulphonic acids, but instead the mixture may be converted into a mixture of anthrarufin and chrysazin, and by successive sulphonation, nitration, and reduction, either with stannous chloride or with sodium sulphide, a useful dye of Alizarin Saphirol type obtained.

There is further a general similarity between quinizarin, anthrarufin, and chrysazin as regards the production of acid dyes by condensation with aromatic amines followed by sulphonation. Thus condensation of anthrarufin and *p*-toluidine followed by sulphonation of the product leads to the dyestuff *Anthraquinone Violet*, and similar products may be prepared from chrysazin. Chrysazin is not a mordant dyestuff, but dinitro, dihydroxylamino, and diaminochrysazins can be applied to mordanted fabrics. The dinitro compound dyes chromed wool blue.

Literature.—Schrubsdorff (Ber. 36, 2936); Wobling (Ber. 36, 2941); Nölting (Chem. Zeit. 1910, 977; J. Soc. Chem. Ind. 1898, 372; 1900, 342; 1906, 314).

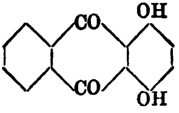
Dihydroxyanthraquinone (?), described as isochrysazin, has been obtained by Lifschütz (Ber. 17, 897) by treating dinitroanthraquinone with concentrated sulphuric acid.

It crystallises from alcohol and ether in deep-red needles, which melt at 175°–180°. It dissolves in alkalis and in ammonia with a reddish-violet colour, and in sulphuric acid with a reddish yellow colour. When heated it sublimes readily, and at a comparatively low temperature, in orange-red plates or needles. It does not dye mordanted cloth.

The *diacetyl compound* melts at 160°–165°.

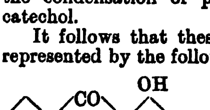
In view of the fact that dinitroanthraquinone is a mixture of the 1 : 5- and 1 : 8-isomerides, it appears very probable that this supposed dihydroxyanthraquinone is a mixture.

Constitution of the dihydroxyanthraquinones. The synthesis of quinizarin from phthalic anhydride and quinol establishes its constitution as 1 : 4-dihydroxyanthraquinone

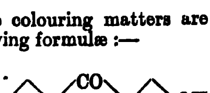


Further alizarin and hystazarin are produced by the condensation of phthalic anhydride with catechol.

It follows that these colouring matters are represented by the following formulæ :—



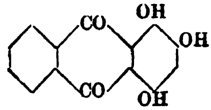
I.



II.

The synthesis of alizarin from hemipinic acid is conclusive evidence that the formula I. represents alizarin, and consequently II. is the structure of hystazarin.

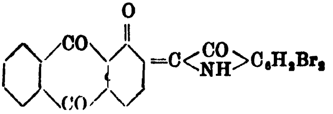
Again, purpurin is produced by the oxidation of both alizarin and quinizarin, and must therefore be 1 : 2 : 4-trihydroxyanthraquinone



On reduction it yields neither alizarin nor quinizarin, but purpuroxanthin, which is obviously 2 : 4-dihydroxyanthraquinone (the same position as 1 : 3).

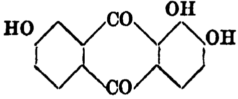
Similar arguments can be developed with respect to the remaining isomerides of alizarin.

Alizarin Indigo G (Bayer, D. R. P. 237199)



This is a vat dye obtained by the condensation of dibromoisatin chloride with α-anthrol. The solution in sodium hydrosulphite is yellow-brown, and cotton is dyed in pure greenish-blue shades of excellent fastness.

III. **Trihydroxyanthraquinones: Anthrapurpurin, *Iso*purpurin, Hydroxy*iso*anthraflavic acid.** 1 : 2 : 7-Trihydroxyanthraquinone



This important colouring matter is contained in crude artificial alizarin. It is formed by fusing β-anthraquinonedisulphonic acid, *iso*anthraflavic acid, metabenzdihydroxyanthraquinone, or α-dibromanthraquinone with potash.

The preparation of this substance is a somewhat tedious process, dependent on the fact that anthrapurpurin differs from alizarin in the behaviour of its alumina lake. The former, on treatment with an alkaline carbonate, is dissolved, whilst the alizarin lake remains unattacked. The solution containing the anthrapurpurin is filtered from the alizarin lake, heated to boiling, and acidified with hydrochloric acid. The anthrapurpurin thus obtained is purified by conversion into its difficultly soluble sodium compound, and from this, by precipitation with barium chloride, the barium salt is obtained, which is decomposed with hydrochloric acid. The precipitate is collected on a filter, well washed with water and recrystallised from glacial acetic acid.

As already mentioned above, the manufacture of alizarin always implies the production of a certain amount of the anthraquinone 2 : 6- and 2 : 7-disulphonic acids, and the methods by which these substances are isolated have been discussed. On fusion with alkali it is possible to obtain from these sulphonic acids either the corresponding dihydroxyanthraquinones or, on the other hand, to imitate the alizarin fusion and to introduce a further hydroxyl group. In this way anthrapurpurin and flavopurpurin are produced on a commercial scale. The temperature of the fusion must be considerably higher than that which suffices for the conversion of 'silver salt' into alizarin. The conversion of anthraflavic acid and isoanthraflavic acid into corresponding trihydroxyanthraquinones occurs with very different rapidity, the former substance (which yields anthrapurpurin) reacting sluggishly. Wedekind and Co. (D. R. P. 194945) fuse 100 parts of anthraflavic acid with 50 parts of saltpetre and 1500 volume parts of caustic lye (b.p. 185°) at 215°–225°. Bayer (D. R. PP. 205097 and 223103) employ only a 20 p.c. caustic soda solution and a temperature of 180°–200°. If, however, in fusing the disulphonic acids with alkali the temperature necessary is quickly reached, it is probable the reaction first leads to alizarin sulphonic acids, which are subsequently changed to anthrapurpurin and flavopurpurin. The following example of the proportions used in the fusion may be given :—

Two cbm. of the disulphonic acids liquor (obtained as already described) containing solid in suspension and with a dry content amounting to 27·65 p.c., equivalent to 553 kg. of the sodium salts, is mixed with 180 kg. saltpetre and 1012 litres of soda lye of 45° Bé. (containing 618 kg. NaOH). This mixture is heated nearly to boiling, and three drums of solid caustic soda then added (795 kg.). This procedure ensures the rapid heating of the mixture which is so necessary to obtain good results. The reaction is carried out in apparatus similar to that used for the preparation of alizarin, and the operation of fusion occupies 48 hours. The product is worked up much in the same way as alizarin, and is brought into commerce in the form of a paste. The impurity present in these trihydroxyanthraquinones is usually anthraflavic acid, and this may be separated by taking advantage of the insolubility of the sodium salt of anthraflavic acid in sodium hydroxide solution of 10°–12° Bé In order to separate the anthraflavic acid it is accordingly merely necessary to dilute to this concentration and filter off the sodium anthraflavate.

Anthrapurpurin crystallises in orange-coloured needles, which melt above 330°, and, when carefully heated, sublime in long red needles. It dissolves in alkalis with a violet colour ; the solution shows the same absorption spectrum as alizarin

With acetic anhydride anthrapurpurin forms a triacetate $C_{14}H_5(C_2H_3O)_3O_5$, which crystallises in yellow needles, melting at 220°.

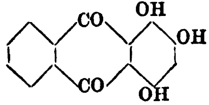
By careful hydrolysis the triacetyl derivative may be converted to a diacetyl derivative, a micro-crystalline pale yellow powder which melts at 175°–178°, and is also obtained by the moderated acetylation of anthrapurpurin. This substance possesses therapeutic value. When heated with ammonia, anthrapurpurin is converted into anthrapurpurinamide

$$C_{14}H_5(NH_2)(OH)_2O_2$$

Anthrapurpurin has the same affinity for mordants as alizarin ; the colours it produces are also analogous to some extent, as it produces reds with alumina, purples and blacks with iron mordants. There is, however, a considerable difference in the shade of colour produced, the reds being much purer and less blue than those of alizarin, whilst the purples are bluer and the blacks more intense. When used in Turkey-red dyeing it produces very brilliant colours of a scarlet shade, which are of remarkable permanence.

Literature.—Perkin (Chem. Soc. Trans. 25, 659; 26, 425; 29, 851); Caro (Ber. 9, 682); Schunck and Römer (Ber. 9, 679; 10, 972, 1823; 13, 42); Rosenstiehl (Bull. Soc. chim. 29, 405); Auerbach (J. 1874, 488); Ullmann (Enzyk, der Tech. Chem. under Alizarin).

Purpurin 1 : 2 : 4-Trihydroxyanthraquinone



Purpurin occurs along with alizarin in madder, probably as a glucoside. In order to separate it from alizarin, the mixture of the two substances is repeatedly recrystallised from a hot solution of alum, in which purpurin is more soluble than alizarin, or the mixture is dissolved in caustic soda and the solution saturated with carbonic acid. This precipitates the alizarin, but not the purpurin.

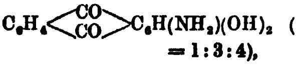
Purpurin is obtained when alizarin or quinizarin (1 pt.) is heated with pyrolusite (1 pt.) and concentrated sulphuric acid (8–10 pts.) at 160°. The oxidation of alizarin to purpurin is also effected by the action of ammonium persulphate in sulphuric acid containing sulphuric anhydride. α-Aminoalizarin is changed to purpurin by the action of nitrous acid in sulphuric acid solution, or by the action of sulphuric acid alone at 150°. Alizarin yields purpurin by the action of sulphuric acid at 225°. Alizarin sulphonic acid is oxidised by heating with sulphuric acid and a nitrate to purpurin sulphonic acid, and the latter yields purpurin on heating under pressure with dilute mineral acids. Anthraquinone-1-sulphonic acid if heated with oleum containing a high percentage of SO_3 is changed to a sulphuric ether which is hydrolysed by heating with sulphuric acid, and the product is purpurin-1-sulphonic acid. This dyes alum mordanted wool in red shades, and may be converted into purpurin.

Purpurin crystallises from dilute alcohol in long orange-coloured needles, which contain 1 mol. H_2O. The pure substance begins to sublime at 150°, and melts at 253°. It is slightly soluble in water, forming a deep yellow solution; in alkalis it dissolves with a purple-red colour; in alkaline carbonates with a red colour. The solution in alkalis shows two marked absorption bands in the green. Purpurin also dissolves readily in ether, carbon disulphide, benzene, and acetic acid; these solutions give two absorption bands, one at F and the other near E; the solution in sulphuric acid shows another line in the yellow. When boiled with acetic anhydride it yields a triacetate,

$$C_{14}H_5(C_2H_3O)_3O_5,$$

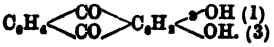
which crystallises in yellow needles, melting at 192°–193°.

Aqueous ammonia at 150° converts purpurin into purpurinamide



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H(NH_2)(OH)_2 \quad (OH:OH:NH_2 = 1:3:4),$$

which, when boiled with ethyl nitrite, yields purpuroxanthin,

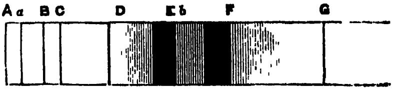


$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_2{<}\begin{matrix}OH\ (1)\\OH.\ (3)\end{matrix}$$

Purpuroxanthin is also the product when purpurin is reduced with either alkaline stannous chloride or sodium amalgam. If, however, zinc-dust be employed as the reducing agent in weakly alkaline, neutral, or acid solution, then the leuco- compound of quinizarin is obtained. Purpurin is converted into 2-anilino-1 : 4-dihydroxyanthraquinone when heated with a mixture of aniline and aniline hydrochloride. A certain amount of dianilino-hydroxyanthraquinone is produced at the same time.

Purpurin dyes fabrics much in the same way as alizarin and anthrapurpurin, there being, however, a difference in the shades. The reds produced by purpurin are much yellower, and the browns (with chrome mordant) much more intense than are produced either by alizarin or anthrapurpurin.

The following figure shows the absorption spectrum of a solution of purpurin in aluminium sulphate :—

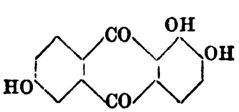


Alizarin Blue Black B, 3B, G (Bayer), is obtained by the condensation of purpurin with aniline followed by sulphonation of the product. The dye is applied on a chromium mordant.

Purpurin-3 : 8-disulphonic acid is obtained by heating the potassium salt of anthraquinone-1 : 5-disulphonic acid with boric acid and 40 p.c. oleum under 6–7 atmos. pressure. The purpurin disulphonic acid so produced forms a potassium salt which crystallises from dilute hydrochloric acid in yellow red leaflets which have a bronze lustre. Heated at 180° with 70 p.c. sulphuric acid the disulphonic acid is changed to *purpurin*-8-*sulphonic acid*, and in the presence of a mercury salt into purpurin itself (Bayer, D. R. P. 172688). The action of alkali sulphites on purpurin leads to the production of *purpurin*-3-*sulphonic acid*, which may readily be reconverted into purpurin.

3-Chloropurpurin is formed along with *dichloropurpuroxanthin* by the action of sulphuryl chloride on a sulphuric acid solution of 2 : 4-dihydroxybenzoylbenzoic acid in the presence of boric acid. It crystallises in deep red needles melting at 270°–273° (Mettler, Ber. 45, 800).

Flavopurpurin. 1 2 : 6-Trihydroxyanthraquinone

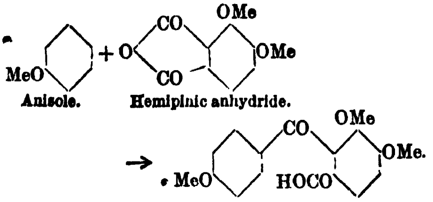


Flavopurpurin occurs in commercial artificial alizarin, but is with difficulty isolated from this product, owing to the fact that its chemical properties agree so closely with those of anthrapurpurin, which is also nearly always present in artificial alizarin, that it can only with difficulty be separated from this substance.

It is prepared by fusing β-anthraquinonedisulphonic acid or anthraflavic acid with potash or soda with or without the addition of a nitrate or chlorate. The details of the technical preparation have been discussed above under *Anthrapurpurin.*

It may be synthesised by the following series of reactions :—

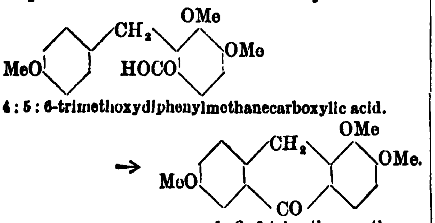
Hemipinic anhydride condenses with anisole in the presence of anhydrous aluminium trichloride, yielding the trimethyl ether of 4 : 5 : 6-trihydroxybenzoyl benzoic acid.



Anisole. Hemipinic anhydride.

Trimethoxybenzoylbenzoic acid.

This benzophenone derivative is reduced by zinc-dust and concentrated hydrochloric acid, and the product is 4 : 5 : 6-trimethoxydiphenylmethanecarboxylic acid, which is changed by sulphuric acid to 1 : 2 : 6-trimethoxyanthrone.



4 : 5 : 6-trimethoxydiphenylmethanecarboxylic acid.

1 : 2 : 6-trimethoxyanthrone.

1 : 2 : 6-trimethoxyanthrone crystallises from benzene in small needles melting at 170°. It is oxidised by chromic acid in glacial acetic acid solution to the trimethyl ether of flavopurpurin, which consists of yellow needles, crystallises from acetic acid, and melts at 225°. The trimethyl ether is hydrolysed to flavopurpurin by the action of aluminium chloride at 210°.

Flavopurpurin crystallises from alcohol in anhydrous yellow needles, sparingly soluble in water, but readily soluble in cold alcohol. Its melting-point lies above 330°.

It dissolves in caustic alkalis with a purple colour; the solution shows two absorption bands, one in the blue and the other near the red, but a little further removed than the alizarin band.

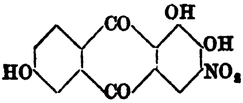
Flavopurpurin dyes mordanted fabrics similarly to alizarin, there being, however, a slight difference in the shades produced. The red shade is somewhat duller and yellower; the brown shade is also yellower. Flavopurpurin dyes wool mordanted with tin crystals and cream of tartar a bright yellowish orange.

When heated with acetic anhydride, flavopurpurin yields a triacetate $C_{14}H_5(C_2H_3O)_3O_5$, which crystallises from alcohol in golden-yellow plates melting at 238°.

Direct methylation converts flavopurpurin into a dimethyl ether, but, as in the case of alizarin, a trimethyl ether is obtained by oxidation of the product of methylation of deoxyflavopurpurin (Graebe, Ber. 38, 152).

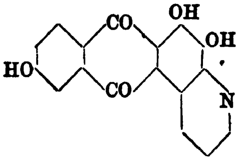
Alizarin Red 3 W. S. is the sodium salt of the monosulphonic acid of flavopurpurin.

Alizarin Orange G. Nitroflavopurpurin.



is similarly constituted to β-nitroalizarine. It is obtained by the nitration of flavopurpurin with ordinary nitric acid. Fast orange shades can be produced by applying this compound with an aluminium mordant.

On treatment with glycerol and sulphuric acid a trihydroxyanthraquinone quinoline of the constitution

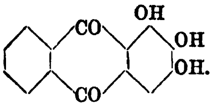


is produced, the bisulphite compound of which is the dyestuff **Alizarin Black P.**

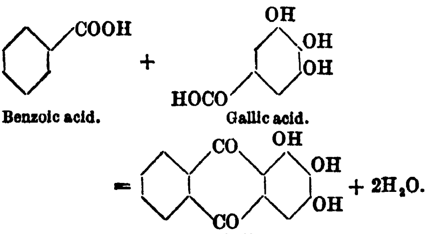
It is used for producing a fast violet grey to black in cotton-printing.

Literature.—Caro (Ber. 9, 682); Schunck and Römer (Ber. 9. 679; 10, 1823; 13, 42): Bistrzycki and Yssel de Schepper (Ber. 31, 2798).

Anthragallol. 1 : 2 : 3-Trihydroxyanthraquinone.



Anthragallol does not itself occur in nature, but its three isomeric dimethyl ethers have been found in Chay root (*Oldenlandia umbellata*). Anthragallol is formed when a mixture of gallic acid (1 pt.), benzoic acid (2 pts.), and sulphuric acid (20 pts.) are heated to 125° for eight hours.



Benzoic acid. Gallic acid.

Anthragallol.

The product is poured into water, well washed, and recrystallised from alcohol.

It is also obtained from 1 : 3-dinitro-2-hydroxyanthraquinone (the nitration product of 2-hydroxyanthraquinone) by reduction in strongly alkaline solution. Or 1 : 3-diamino-2-hydroxyanthraquinone may be converted to anthragallol by heating with hydrochloric acid under pressure.

Anthragallol crystallises in yellow needles which, when heated to 290°, sublime without melting. It is sparingly soluble in water, chloroform, or carbon disulphide; readily soluble in alcohol, ether, or glacial acetic acid.

It dissolves in alkalis forming a green solution.

Its triacetate $C_{14}H_5(C_2H_3O)_3O_5$ melts at 171°-173°.

With an excess of ammonia anthragallol reacts, forming anthragallolamide, 1-amido-2 : 3-dihydroxyanthraquinone.

Literature.—Seuberlich (Ber. 10, 39).

By the action of dimethyl sulphate in boiling nitrobenzene and in presence of anhydrous sodium carbonate anthragallol yields the *dimethyl ether* which occurs in orange needles melting at 159°-160°, and forms an *acetyl derivative* melting at 167°. Concentrated sulphuric acid hydrolyses this substance at 100° and forms a monomethyl ether melting at 233° (acetyl derivative, m.p. 184°), whilst the action of a great excess of methyl sulphate and sodium carbonate at 180° converts either the monomethyl ether or the dimethyl ether into anthragallol trimethyl ether, which is lemon-yellow and melts at 168° (Böck, Monatsh. 23, (9) 1008).

Hydroxyanthrarufin, 1 : 2 : 5-Trihydroxyanthraquinone. This substance is readily obtained by heating anthrarufin with a mixture of sodium and potassium hydroxides at 180°-185° in the presence of water and sodium nitrate. It is also produced when alizarin is dissolved in 70 p.c. oleum to which boric acid has been added, and the mixture agitated at 30°-35° until a pure violet solution has been obtained. The sulphuric ester so produced is then hydrolysed in the usual manner. The two methods combined determine the constitution of this trihydroxyanthraquinone which crystallises from acetic acid in red needles melting at 273°-274°, and forms a triacetate melting at 227°. Hydroxyanthrarufin is a valuable mordant dyestuff.

Literature.—Liebermann and Boeck (Ber. 11, 1716); Liebermann and Dehnst (Ber. 12, 1289); M. L. B. (D. R. PP. 195028 and 196980); By (D. R. P. 156960); Ziegler (J. pr. Chem. 86, 297).

Hydroxychrysazin, 1 : 2 : 8-trihydroxyanthraquinone. Chrysazin is converted into this substance by fusion with aqueous sodium and potassium hydroxides in presence of sodium nitrate at 180°. It crystallises in orange needles melting at 230°, and forms a triacetyl derivative melting at 219°. The *dimethyl ether* forms light yellow needles melting at 157°.

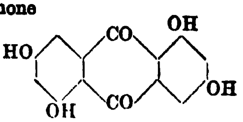
1 : 4 : 8-Trihydroxyanthraquinone. Oxidation of chrysazin by means of 80 p.c. oleum and boric acid at 25°-35° yields the sulphuric ester of this isomeride, and on heating with ordinary sulphuric acid the substance is obtained. It separates from pyridine in brown-red needles with green metallic reflex and dissolves in aqueous sodium hydroxide, and also in sulphuric acid to a violet solution (By, D. R. P. 161026). This compound is also obtained by the reduction of Alizarin Bordeaux.

1 : 3 : 8-Trihydroxyanthraquinone. The trihydroxyanthraquinone obtained from rhein through its amide and dihydroxyaminoanthraquinone (Oesterle, Arch. Pharm. 1912, 250, 301) is not identical with hydroxychrysazin, and since rhein must be either chrysazin-2- or 3-carboxylic acid, this fact favours the latter theory. 1 : 3 : 8-Trihydroxyanthraquinone melts at 277°-278°, and yields a triacetyl derivative melting at 197°-198°.

1 : 4 : 6-Trihydroxyanthraquinone is the chief product when 4-aminophthalic anhydride is heated with quinol and concentrated sulphuric acid at 170°-190°.

IV. Tetrahydroxyanthraquinones.

Anthrachrysone 1 : 3 : 5 : 7-Tetrahydroxyanthraquinone

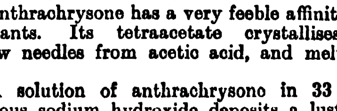


The preparation of this body is effected by heating 3 : 5-dihydroxybenzoic acid with 10 parts of sulphuric acid for 3 to 5 hours.

The substance consists of silky yellow needles when crystallised from alcohol, or it can be sublimed with partial decomposition in leaflets. It does not melt at 360°.

Anthrachrysone has a very feeble affinity for mordants. Its tetraacetate crystallises in yellow needles from acetic acid, and melts at 253°.

A solution of anthrachrysone in 33 p.c. aqueous sodium hydroxide deposits a lustrous vivid red sodium salt which is converted into a crystalline ammonium salt by ammonium chloride. A crystalline potassium salt is also known, and when this is heated with methyl sulphate at 180°-190° it is converted into anthrachrysone dimethyl ether which crystallises from nitrobenzene in golden brown columns and forms a sodium salt crystallising in orange-red needles. The diacetyl derivative melts at 256°. The methylation also results in the production of a small proportion of anthrachrysone tetramethyl ether which crystallises in golden-yellow prisms melting at 294° (Fischer and Ziegler, J. pr. Chem. 1912, ii. 86, 297). Anthrachrysone condenses with secondary bases, such as diethylamine, and formaldehyde, with the production of tetraalkyldiaminodimethylanthrachrysones. The compound



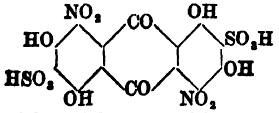
is obtained from diethylamine (M. L. B., D. R. P. 188189).

Literature.—Hohenemer (Ber. 35, 2305); Barth Senhofer (Annalen, 164, 109); Noah (Ber. 19, 755).

1 : 3 : 5 : 7-Tetrahydroxyanthraquinone-2 : 6-disulphonic acid is obtained by heating anthrachrysone with an excess of fuming sulphuric acid (D. R. P. 70803). It forms a characteristic *sodium salt* which crystallises in glistening coppery platelets. By the action of chlorine it is converted into a *dichloro- derivative*, whilst, on the other hand, sodium hypochlorite converts the sodium salt into *dichloroanthrachrysone* by elimination of the sulphonic groups. *Dibromoanthrachrysone* is obtained by bromination of anthrachrysone in acetic acid solution. It melts at above 290°, and occurs in orange-red needles. The action of bromine on a solution of the disulphonic acid in dilute acetic acid is to produce *tetrabromoanthrachrysone*, dark-red needles melting above 300°.

Various dyestuffs are derived from anthrachrysone.

Dinitroanthrachrysonedisulphonic acid



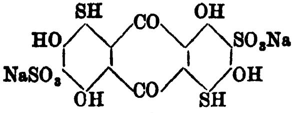
is prepared by sulphonation, followed by nitration of anthrachrysone.

It is a fast brown wool dye.

On reduction it yields diaminoanthrachrysonedisulphonic acid, which dyes wool violet from an acid-bath, or blue on a chromium mordant.

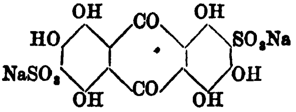
If, however, the reduction is carried out in alkaline solution with sodium sulphide, then the dyestuff **Acid Alizarin Green B and G** results.

The constitution of this product is



It dyes chromed wool a fast, pure green.

Acid Alizarin Blue BB and GR



is obtained by boiling diaminoanthrachrysone disulphonic acid with alkali. A red shade is produced on wool from an acid-bath, which on chroming develops a beautiful blue, exceedingly fast to light milling, acids or alkalis.

8-Nitro-4-anilino-1 : 3 : 5 : 7-tetrahydroxyanthraquinone-2 : 6-disulphonic acid is obtained in the form of its trisodium salt (dark bluish-violet crystals with coppery lustre) by heating a solution of 4 : 8-dinitro-1 : 3 : 5 : 7-tetrahydroxyanthraquinone-2 : 6-disulphonic acid in aqueous sodium carbonate with aniline. A similar replacement of the nitroxyl by anilino occurs with the unsulphonated dinitro- compound (Heller and Skraup, Ber. 46, 2703; D. R. P. 71964).

Rufiopin, 1 : 2 : 5 : 6-Tetrahydroxyanthraquinone.

This tetrahydroxyanthraquinone is obtained by heating opianic or hemipinic acids with sulphuric acid at 180°.

Also by fusing the disulphonic acid of anthrarufin with potash.

It forms a reddish-yellow crust from ether, and can be sublimed in orange needles.

It gives a violet-red solution in dilute alkalis or in sulphuric acid. A curious property of rufiopin is its stability towards fusion with potash.

The substance is of no value as a dyestuff, since it gives only dull-brown shades with mordants.

Literature.—Liebermann and Chojnacki (Annalen, 162, 323); D. R. P. 103988.

α- and β-Hydroxyanthragallols.

A mixture of these substances is produced when equimolecular proportions of gallic and *m*-hydroxybenzoic acids are heated at 150°, with 10 parts of sulphuric acid for twenty hours.

The product is poured into water and the dried precipitate extracted with alcohol. This extract is evaporated and the residue treated with hot benzene. The α- compound passes into solution, whilst the β- remains undissolved.

α-Hydroxyanthragallol crystallises from alcohol in golden yellow micro- needles. It forms a green solution in alkalis, whilst that in sulphuric acid is violet, and shows two absorption bands between F and D. With mordants it behaves similarly to rufigallic acid.

Its tetraacetyl derivative melts at 207°–209°.

β-Hydroxyanthragallol crystallises from alcohol and occurs in red needles. Its brown-red solution in sulphuric acid shows two absorption bands between E and H.

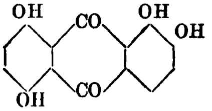
The tetra-acetate crystallises from glacial acetic acid in lemon-yellow tables of m.p. 189°.

Literature.—Noah (Annalen, 241, 270).

1 : 2 : 3 : 4-Tetrahydroxyanthraquinone is obtained by heating anthragallol with sulphuric acid in the presence of boric acid at 200°–240°. It consists of green needles soluble in both alkalis and sulphuric acid with red colour. The tetraacetyl derivative melts at 205°.

Literature.—Bayer and Co. D. R. P. 86968.

Alizarin bordeaux (Quinalizarin). 1 : 2 : 5 : 8-Tetrahydroxyanthraquinone



Alizarin bordeaux is by far the most important of the tetrahydroxyanthraquinones.

It has been obtained by the hydrolysis of its dimethyl ether (*see* below) with a solution of hydrochloric acid in acetic acid at 200°.

It is prepared by heating alizarin (1 pt.) with sulphuric acid (10 pts. containing 80 p.c. SO_3) for four days at 25°–50°. This yields the sulphuric acid ester of alizarin bordeaux, to obtain which the reaction product is rendered alkaline and then boiled with an excess of hydrochloric acid.

It is found that the oxidation of alizarin occurs more readily in presence of boric acid.

Alizarin bordeaux can be obtained in deep red needles with green metallic reflection.

On an aluminium mordant it produces bordeaux shades; violet blue on chromium.

The tetraacetate crystallises from chloroform-alcohol in micro- needles of m.p. 201°.

Dimethyl ether.

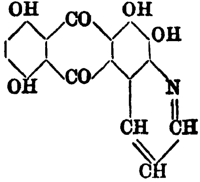
This substance is synthesised by heating hemipinic acid and quinol with sulphuric acid to 130°.

The brown-red micro leaflets obtained by crystallisation from benzene melt at 225°–230°.

Literature.—Schmidt (J. pr. Chem. [2] 43, 239); Liebermann and Wense (Annalen, 240, 299).

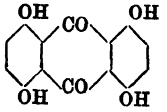
Alizarin Green S (B).

Alizarin blue can be oxidised by means of sulphur trioxide, and the product on treatment with sulphuric acid gives a dihydroxyalizarin blue of the probable constitution



Alizarin Green S (B) is the bisulphite compound of this tetrahydroxyanthraquinone quinoline. It dyes very fast bluish-greens on chromed wool.

1 : 4 : 5 : 8-Tetrahydroxyanthraquinone



This substance has been obtained by the action of sulphuric acid on *pp*-dinitroanthrarufin (By, D. R. PP. 125579, 162033), but the following method establishes the constitution of the substance :—

5 : 8-Dichloroquinizarin is heated for 20 hours at 250° with milk of lime and copper. The product is acidified with hydrochloric acid, and the substance may then be collected and crystallised from a mixture of benzene and ligroin. The brown needles melt at 246°, and dissolve in alkaline solutions with a cornflower-blue colouration. The sulphuric acid solution exhibits two bands in the red and yellow respectively.

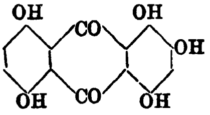
It is interesting that this tetrahydroxyanthraquinone has powerful mordant dyestuff properties (Frey, Ber. 45, 1361).

The tetraacetyl derivative forms light yellow needles melting at 250° with decomposition, and the difficultly soluble blue potassium salt is converted by methyl sulphate at 180° into a tetramethyl ether, which crystallises in lustrous orange leaflets and melts at 317° (Fischer and Zeigler, J. pr. Chem. 1912, ii. 86, 297).

Dihydroxychrysazins. Two isomeric tetrahydroxyanthraquinones have been obtained from chrysazin. The first (Schrubsdorff, Ber. 35, 2936) by fusion of chrysazin with potassium hydroxide. This isomeride sublimes *in vacuo*, forms dark-red needles melting at 217°, and intensely colours ordinary mordants. Its acetate melts at 195°. The second compound (Wobling, Ber. 36, 2941) is obtained by fusing chrysazin disulphonic acid with alkali. This melts at 292°, and also colours mordants. Its tetraacetyl derivative melts at 233°.

V. Pentahydroxyanthraquinones.

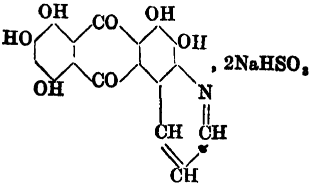
Alizarin cyanine R. 1 : 2 4 : 5 : 8-Pentahydroxyanthraquinone



This valuable substance is obtained by the oxidation of alizarin bordeaux with pyrolusite in sulphuric acid solution. The sulphonic acid ether so produced is hydrolysed by boiling with dilute acid. This oxidation is entirely analogous to that by which purpurin is produced from alizarin. The substance crystallises in bronze-coloured leaflets from nitrobenzene. The blue solution in concentrated sulphuric acid exhibits red fluorescence.

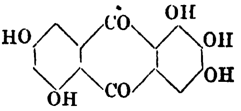
Alizarin cyanine R. yields a handsome blue chromium lake.

Alizarin Indigo Blue S.



is the bisulphite compound of the pentahydroxyanthraquinone quinoline, obtained by the further oxidation of alizarin Green S (B) with concentrated sulphuric acid at 200°. It yields fast indigo-blue shades on crome mordanted wool.

Dihydroxyanthragallol. 1 : 2 : 3 : 5 : 7-Pentahydroxyanthraquinone



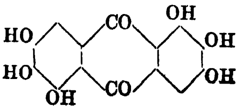
Equimolecular amounts of gallic acid and 3 : 5-dihydroxybenzoic acid are heated to 160° for ten minutes with ten times their weight of sulphuric acid. The product contains dihydroxyanthragallol, rufigallic acid, and anthrachrysone. In order to separate them, advantage is taken of the fact that only dihydroxyanthragallol pentaacetate is soluble in alcohol. The acetate so obtained is hydrolysed with cold sulphuric acid.

Dihydroxyanthragallol crystallises from alcohol in small red needles, which do not melt at 360°. The substance is similar in tinctorial properties to rufigallic acid.

The pentaacetate melts at 229°.

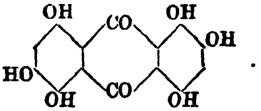
Literature.—Noah (Annalen, 241, 275).

VI. Hexahydroxyanthraquinones. Rufigallol. Rufigallic acid, 1 : 2 : 3 : 5 : 6 : 7-Hexahydroxyanthraquinone



Rufigallic acid is produced when gallic acid is heated with concentrated sulphuric acid at 140°. It may be sublimed in yellow needles. A violet solution is obtained with alkalis, red with sulphuric acid. Baryta produces a blue insoluble precipitate. Alizarin is obtained by the reduction of rufigallic acid with sodium amalgam. The substance is a good example of a polygenetic dyestuff, and yields with aluminium, iron, and chromium mordants, red, violet, and brown respectively. The colours are, however, not pure in tone.

Anthracene Blue. 1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone



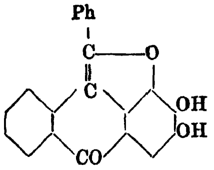
Anthracene blue is an important dyestuff, and can be obtained from erythroxyanthraquinone, anthrarufin, or anthrachrysone, by the oxidising action of sulphur trioxide in sulphuric acid in the presence of boric acid.

It is best prepared by the action of 40 p.c. oleum with or without the addition of sulphur on 1 : 5-dinitroanthraquinone, and treatment of the product with ordinary sulphuric acid.

The solution in concentrated sulphuric acid is violet-blue and shows a brown fluorescence. The aluminium lake is violet and the chromium lake blue.

Its disulphonic acid is Acid alizarin blue B B, mentioned above, and prepared from anthrachrysone.

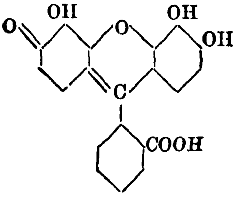
Benzoin Yellow



is prepared by the condensation of benzoïn with gallic acid under the influence of sulphuric acid.

It dyes wool on a chromium mordant a fast yellow (except to light).

Galleïn $C_{20}H_{12}O_7$



Galleïn is formed by heating pyrogallol with phthalic anhydride.

Preparation.—A mixture of 1 part of phthalic anhydride and 2 parts of pyrogallol are heated to 190°–200°, the product dissolved in alcohol, and the colouring matter precipitated by the addition of water. The crude galleïn thus obtained is dissolved in alcohol, reprecipitated with water, and, after repeating this operation a few times, converted into the acetate by heating with acetic anhydride. This is recrystallised several times, and decomposed with potash.

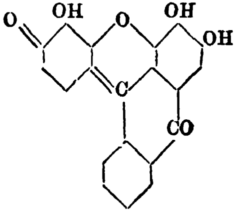
Galleïn crystallises from alcohol in small greenish crystals. It is insoluble in chloroform and benzene, sparingly soluble in water and ether, readily soluble in alcohol, forming a dark-red solution. It dissolves in cold concentrated sulphuric acid without change; on warming the solution cœruleïn is formed.

Galleïn dissolves in small quantities of potash or soda with a red colour; excess of alkali produces a blue solution. Heated to 150° with acetic anhydride galleïn yields a tetracetate of hydrogalleïn.

Galleïn (often called anthracene violet) is sold in the form of a reddish-brown powder, or a 10 p.c. paste; not very soluble in cold water, but readily so in hot. With all the usual alizarin mordants galleïn produces purple colours, which are fast to light and soap; those obtained by the use of chromium and iron are bluish, those with tin reddish, those with aluminium intermediate in tone.

Literature.—Baeyer (Ber. 4, 457 and 663); Buchka (Annalen, 209, 261); Orndorff and Brewer (Amer. Chem. J. 1901, 97).

Cœrulein $C_{20}H_{10}O_6$



Cœrulein is prepared by heating 1 part of gallein and 20 parts of sulphuric acid to 200°, and precipitating the colouring matter by adding a large quantity of water. It is thus obtained as a bluish-black mass, which, when rubbed, acquires a metallic appearance. It is almost insoluble in water, ether, and alcohol, more readily soluble in acetic acid.

It dissolves in alkalis with a green colour, in acids with an olive-brown colour. With bisulphite of soda cœruleïn forms an easily soluble compound. With acetic anhydride it forms a triacetate. Cœrulein (anthracene green) is sold in two forms, either as a bluish-black paste containing 10–20 p.c. cœrulein, or as a black powder.

The former is insoluble in water, the latter, known as cœruleïn S, is soluble in water, and is indeed a bisulphite compound of cœruleïn.

Cœruleïn is mostly employed in calico-printing for producing very fast olive-green shades. Whatever the mordant used, only different shades of olive-green are produced.

Literature.—Baeyer (Ber. 4, 556, 663); Orndorff and Brewer (Amer. Chem. J. 1901, 97).

F. H. G., W. H. P. and R. R.

ALIZARIN (Natural) *v.* CHAY ROOT and MADDER.

ALIZARIN AND METHYL ETHER *v.* CHAY ROOT.

ALIZARIN BLACK, -BLUE, -BORDEAUX, BROWN, -CARDINAL, -CYANINE, -GARNET, GREENS, -MAROON, -ORANGE, -REDS, -SAPHIROL *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ALIZARIN YELLOW *v.* AZO- COLOURING MATTERS; KETONES.

ALKALI ALBUMIN *v.* PROTEINS.

ALKALI BLUE. *Nicholson's blue. Sodium triphenyl-rosaniline sulphonate* (*v.* TRIPHENYL METHANE COLOURING MATTERS).

ALKALI BROWNS, -YELLOW *v.* AZO- COLOURING MATTERS.

ALKALIMETRY *v.* ACIDIMETRY.

ALKALI WASTE *v.* *Soda manufacture,* art. SODIUM.

ALKALOIDS. The alkaloids are nitrogenous basic carbon compounds occurring mostly in plants, but a few animals, *e.g.* the salamander, contain bases similar in every respect to the typical vegetable alkaloids. The exact demarcation of the group is difficult; generally the alkaloids may be said to contain heterocyclic nitrogen, to be soluble in solvents immiscible with water and to have a complicated molecular structure. These characters are, as a rule, not possessed by the simpler amines and betaines derived from the amino- acids of proteins, nor by choline and other bases of general biological importance, which, in contradistinction to the typical alkaloids, are not limited to one, or a few, species of plants or animals. For a full account of these amines, betaines, choline, &c., *v.* Barger, The Simpler Natural Bases, Longmans, 1914. A list of books dealing with alkaloids is given at the end of this article.

The discovery of the first alkaloid is due to the German pharmacist Sertürner, who, in 1805, isolated from opium a substance 'morphium,' which he described more fully in 1817 as a basic, salt-forming substance having the principal physiological action of the drug. The discovery of morphine was quickly followed by that of other alkaloids, made chiefly by Pelletier and Caventou. The first volatile alkaloid, coniïne, was isolated in 1827 by Giesecke, and nicotine in 1828 by Posselt and Riemann.

Distribution and mode of formation. No alkaloids have been obtained from algæ and mosses, hardly any from fungi, a few only from vascular cryptogams and gymnosperms, more from monocotyledons, but the vast majority from dicotyledons. Certain large orders, *e.g.* *Compositæ Gramineæ,* are very poor in alkaloids, others such as the *Ranunculaceæ, Solanaceæ, Papaveraceæ* are typically rich. Generally an alkaloid is limited to a single genus or order; berberine, however, occurs in several orders. The total alkaloids of a plant usually consist of a mixture of several bases often closely related, which may be present in very different amounts.

The older view that alkaloids are plastic materials capable of further utilisation by plants has been disproved by Clautriau (Ann. Soc. belge de Microsc. 1894, 18; Ann. Soc. roy. Sci. méd. nat. Bruxelles, 1900, 9), who concludes that they are waste products, only of use as a means of defence on account of their poisonous properties. The amount of alkaloid is generally greatest in the mature plant and in the periphery (bark) or in hibernating parts (root); it varies greatly in different organs. Weight for weight young shoots and leaves may contain more than older ones. For methods of microscopical localisation, *see* Errera, Maistriau, and Clautriau (Ann. Soc. belge de microsc. 1888, 12; Clautriau, *ibid.* 1894, 18).

The mode of origin of alkaloids in plants is not understood and has given rise to much speculation (Czapek, Biochemie der Pflanzen, 1905, ii. 267; Windaus and Knoop, Beitr. chem. Physiol. Path. 1905, 6, 392; Pictet, Arch. Sci. phys. nat. 1905, 243, 329; 1906, 244, 389; Tunmann, Arch. Pharm. 1910, 248, 644; Winterstein und Trier, Die Alkaloide, 1910, 263).; The most fruitful contribution is probably that of Robinson (Trans. Chem. Soc. 1917, 111, 876), who utilises only reactions which can be carried out in the laboratory at the ordinary temperature and shows how several of the principal alkaloids might be built up from ammonia, formaldehyde, ornithine, lysine, and degradation products of carbohydrates, such as citric and acetonedicarboxylic acids. These substances are imagined to undergo aldol and similar condensations, and it is interesting to note that Robinson has actually synthesised tropinone in aqueous solution at room temperature from succindialdehyde, methylamine, and calcium acetonedicarboxylate.

The alkaloids may be classified chemically according to the heterocyclic rings in which nitrogen occurs, as derivatives of pyrrolidine (*e.g.* hygrine), of pyridine (*e.g.* arecoline), of piperidine (*e.g.* piperine), of glyoxaline (*e.g.* pilocarpine), of indole (*e.g.* physostigmine), of quinoline (*e.g.* quinine), and of *iso*quinoline (*e.g.* papaverine); another group contains alkaloids without heterocyclic ring, derivatives of aliphatic amines (*e.g.* narceine). Some alkaloids may be classified under two of the above or under additional groups; thus atropine and cocaine contain both a pyrrolidine and a piperidine ring, caffeine contains a pyrimidine ring in addition to glyoxaline. No chemical classification can be complete, and a large number of alkaloids of insufficiently known constitution have perforce to be arranged according to the plants (or animals) from which they are derived.

Method of extraction and isolation. Generally speaking, alkaloids, whether occurring in the free state or as salts of organic acids, are extracted from the finely powdered material by means of strong spirit. After distilling off the alcohol, the bases are extracted from the residue by dilute acids, liberated by the addition of ammonia or sodium carbonate and extracted by chloroform, ether, or carbon tetrachloride. This gives the total alkaloidal content of the plant, except where a quaternary base is present, when methods similar to those employed for the simpler natural bases, *e.g.* precipitation with mercuric chloride or phosphotungstic acid, are utilised. Certain stable alkaloids may be extracted from a mixture of the finely powdered plant with lime or magnesia by an organic solvent; in other cases (*e.g.* caffeine in tea) extractions with boiling water may be employed.

The 'total alkaloids' of plants obtained by the above methods are mixtures for which no general method of separation can be given. In some cases, caustic soda may be used to separate the phenolic from the non-phenolic bases; in others, fractional extraction of the ether or chloroform solution of the bases with acid brings about a separation; or, again, a fractionation may be effected by regenerating the bases from acid solution by an alkali in the presence of light petroleum or ether, in which only a part of the mixture is soluble. After suitable preliminary treatment on these lines, alkaloids often crystallise as the free base, but if not, it is generally possible to crystallise a salt with a strong or weak acid. A convenient method is to add to the dry ethereal solution of the alkaloid, contained in a tall stoppered cylinder, small amounts of an ethereal or concentrated alcoholic solution of the acid, until no more alkaloidal salt is precipitated, shaking after each addition. If excess of acid is avoided, the flocculent precipitate can be readily washed by decantation and is then crystallised from alcohol, with or without ether. The choice of the proper acid is sometimes of great importance, *e.g.* for physostigmine the salicylate is the best salt, and for ergotoxine the phosphate. Acid oxalates are frequently valuable, whilst aurichlorides are useful for Solanaceous alkaloids and picrates for simple bases, but no general rule can be given. For further information concerning the methods of separating and characterising alkaloids, *see* Allen's Commercial Organic Analysis, vol. vi. 1912, 171–177. and the articles in this dictionary on CINCHONA, IPECACUANHA, and OPIUM ALKALOIDS.

Physical and chemical characters of the alkaloids. Nearly all are solids, and then mostly crystalline; a few (coniine, nicotine) are liquids, and are volatile with steam. In a high vacuum even complex alkaloids may often be sublimed or distilled on a small scale, *e.g.* strychnine. Most alkaloids are optically active; the specific rotation of the free base in a dissociating solvent may differ considerably from that of the ion of a salt in the same solvent, and the two may even have opposite signs (*e.g.* nicotine and its salts) (*cf.* Carr and Reynolds, Chem. Soc. Trans. 1910, 97, 1328).

The majority of the typical alkaloids are insoluble, or very sparingly soluble, in water; their best solvent is alcohol. Usually they are also dissolved by chloroform, less generally by ether, benzene, or amyl alcohol, sometimes by light petroleum. Simple amines, betaines, purine derivatives, and quaternary alkaloids like columbamine, are often more soluble in water than in organic solvents. The aqueous solutions of the alkaloids are often strongly alkaline to litmus, but a few alkaloids which are acid amides (colchicine, caffeine, piperine) are so feebly basic that they may be extracted from acid solution by chloroform, owing to the extensive hydrolysis of their salts. In these cases the salts are mostly not obtainable in a pure crystalline condition. Alkaloidal salts are generally more or less readily soluble in water and in alcohol, but as a rule not in chloroform or ether. Salts of the more complex alkaloids may be very little soluble in excess of the acid, if the latter is highly dissociated (mineral acids or even oxalic acid).

The vast majority of alkaloids are tertiary bases. A few (carpaine, cytisine, ephedrine) are secondary bases; the betaines, berberine, columbamine, &c., are quaternary. Primary bases are only found among amines derived from the amino- acids of protein and not among true alkaloids; they seem to be formed only by bacteria and fungi.

Most of the alkaloids are monacid bases even when they contain several atoms of nitrogen in the molecule. Thus, pilocarpine with two, physostigmine with three, and ergotoxine with five nitrogen atoms are monacid bases. Quinine is the best known example of a *di*-acid alkaloid.

Certain alkaloids or their salts can be hydrogenated in aqueous solution or suspension by means of molecular hydrogen in presence of nickel suboxide, or a colloidal metal of the platinum group, at the normal temperature and pressure or at increased pressures. Thus quinine hydrochloride yields hydroquinine, morphine yields dihydromorphine, and codeine yields dihydrocodeine, whilst cinnamylcocaine gives hydrocinnamylcocaine, an oily liquid decomposed by heat. Strychnine and brucine yield the corresponding dihydrides, and colchicine gives the tetrahydro- derivative. The reduction of these alkaloids may also be effected by nascent hydrogen liberated from formic acid by the action of finely divided metals of the platinum group ($HCOOH=H_2+CO_2$). Quinine, morphine, codeine, and other opium alkaloids may be converted into dihydro- derivatives (Eng. Pat. 10204, 1913; 14247, 1913; D. R. PP. 306939; 230724; 260233; U.S. Pat. 989604; Eng. Pat. 3948, 1912).

General alkaloidal precipitants. *Auric chloride* $AuCl_3$ combines with alkaloidal hydrochlorides to form well-defined aurichlorides of the composition $B,HAuCl_4$, generally sparingly soluble in water, and obtained as pale-yellow precipitates on mixing the gold and alkaloidal chlorides in aqueous solution. The aurichlorides may be recrystallised from alcohol or water acidulated with hydrochloric acid, and are most useful for characterising Solanaceous alkaloids. Occasionally gold chloride is reduced to metallic gold with formation of a red gold sol. The aurichlorides may be analysed by simple ignition, or by combustion, or by decomposition with hydrogen sulphide; in the last case the alkaloid is recovered unchanged by making the filtrate from the gold sulphide alkaline and extracting with chloroform. In a few cases, when alcoholic solutions of gold chloride and of the alkaloid are mixed, stable crystalline salts (auric chloride compounds) of the composition $B,AuCl_3$ are obtained (Dunstan and Ince, Chem. Soc. Trans. 1891, 59, 271). For other aurichloride compounds of abnormal composition, *see* Dunstan and collaborators (Chem. Soc. Trans. 1893, 63, 201, 445; 1900, 77, 57).

Platinic chloride in aqueous solution may precipitate platinichlorides of the composition B_2,H_2PtCl_6, which are generally more soluble than the aurichlorides and are analysed in the same way. In both cases the estimation of the chlorine may be useful.

Picric acid precipitates the solutions of most alkaloidal salts, and the resulting picrates may often be crystallised (from water or alcohol). The alkaloid may be recovered by extracting it from alkaline solution by chloroform, or the picric acid may be removed from acid solution by shaking with ether or benzene. The picric acid is conveniently estimated without the loss of the alkaloid, by nitron (Busch, Ber. 1905, 38, 861).

Picrolonic acid (4-nitro-1-*p*-nitrophenyl-3-methyl-5-pyrazolone) in alcoholic solution behaves similarly (*e.g.* Warren and Weiss, J. Biol. Chem. 1907, 3, 327). The picrolonates are less soluble than the picrates, and are of most use when the base and its picrate are readily soluble in water (histidine, arginine).

The above four precipitants may be used for obtaining crystalline salts for analysis and characterisation. *Mercuric chloride* is occasionally used for the same purpose, but more frequently only for preparative purposes (*see* quaternary bases, above). The following reagents are more sensitive, but generally give only amorphous precipitates, unsuitable for analysis.

Bismuth potassium iodide (Dragendorff's or

Kraut's reagent) has been used for isolating simple water soluble bases, which are recovered by grinding up the brick-red precipitate with freshly prepared lead hydroxide. After filtration the last traces of lead are removed by hydrogen sulphide. Cadmium potassium iodide is also employed as a general alkaloidal precipitant.

Iodine dissolved in aqueous potassium iodide (Wagner's or Bouchardat's reagent) is one of the most general. In dilute solutions a reddish-brown precipitate is formed, which in strong solution aggregates at once to a greenish-black mass, and consists of periodides of variable composition. Many periodides crystallise from alcohol, the crystals being green by reflected, and red by transmitted light (*cf.* herapathite, under QUININE). The recovery of the alkaloid from a periodide may be effected by decolourising with sodium thiosulphate or sulphur dioxide, and shaking out from alkaline solution, or, if this is impossible, grinding up the periodide with 'molecular' copper, when only the iodide of the base remains in aqueous solution.

Potassium mercuric iodide (Mayer's or Tanret's reagent) prepared by adding potassium iodide to mercuric chloride until the mercuric iodide at first precipitated, is re-dissolved, is the best general reagent for detecting alkaloids, and may afford an extremely delicate test. Some alkaloids are most completely precipitated in neutral, others in faintly acid, a few in more strongly acid solution. In very dilute solution only an opalescence is produced, in more concentrated solution a yellowish-white flocculent precipitate occurs, from which the alkaloid may be recovered by suspension in water and passing hydrogen sulphide. In spite of its variable composition, the precipitate may be used to some extent for quantitative purposes (*see* next section).

Tannic acid is merely a colloidal precipitant for complex substances, and precipitates alkaloids, along with some glucosides, peptones, &c.

For a full discussion of the above and other alkaloidal reagents, *see* Allen's Commercial Organic Analysis, 1912, vol. vi. 185–197.

Quantitative estimation of alkaloids. As a rule only the 'total alkaloid' can be determined, although in a few cases of technical importance (*e.g.* cinchona and strychnos alkaloids, *q.v.*) individual alkaloids may be estimated in a mixture. The estimation of the total alkaloid is based on the same principles as the isolation. Keller (Schweiz, Wochenschr. f. Chem. u. Pharm. 1894, 32, 44) mixed the finely powdered drug with magnesium oxide, or moistened it with ammonia, and extracted it with ether, or a mixture of ether and chloroform. An aliquot portion of the extract is shaken with dilute acid, the aqueous solution is rendered alkaline and again shaken several times with ether or chloroform. The alkaloid left on evaporation of the solvent may be weighed, but in most cases it is more satisfactory to titrate it in aqueous or dilute alcoholic solution. Of the various indicators suggested methyl orange and methyl red are theoretically and practically the best in most cases; the latter indicator is said to be quite satisfactory for all the official alkaloids. In special cases haematoxylin is used, and sometimes iodeosin (*see* Allen's Commercial Organic Analysis, vol. vi. 178–183; and von Korczynski, Die Methoden der exakten quantitativen Bestimmungen der Alkaloide, Berlin, 1913). The last-named compilation gives, *i.a.*, all the methods of the German Pharmacopoeia; the U. S. P. may also be consulted. A different principle is involved in the use of Mayer's reagent, which, as a rule, gives much less accurate results. As a titration method this is probably best employed in the form given it by Heikel (Chem. Zeit. 1908, 32, 1149, 1162, 1186, 1212). Potassium mercuric iodide is chiefly useful for quantities too small to be titrated with acid, and should then be used in a nephelometric comparison with alkaloidal solutions of known strength (*cf.* Ramsden and Lipkin, Ann. trop. Med. Parasitol. 1918, 11, 443, who thus estimate quinine in blood and urine with considerable accuracy; minute quantities of other alkaloids can doubtless be estimated in the same way).

Toxicological detection of alkaloids. The principles are similar to those involved in extracting alkaloids from plants, but owing to the minuteness of quantities present and the possible presence of putrefactive and other bases, great care is required. For details of the methods of Stas-Otto, Dragendorff, &c., *see* Wynter Blyth, Poisons, their Effects and Detection, 1909; Kippenberger, Zeit. anal. Chem. 1895, 34, 294; Schmidt, Pharmazeutische Chemie, ii. 1911, 1550–58. Colour reactions are of little use for identifying an unknown alkaloid, especially if impure (*v.* Allen's Commercial Organic Analysis, 1912, vol. vi. 197–201). Pharmacological tests are much more useful.

Bibliography of alkaloids (arranged chronologically).

I. Guareschi. Einführung in das Studium der Alkaloide, transl. from the Italian by H. Kunz-Krause. Berlin, 1896. (Includes many bases, natural and synthetic, not generally regarded as alkaloids.)

J. W. Brühl. Roscoe-Schorlemmer's Lehrbuch der Chemie, vol. viii. 1901. (A complete account, especially theoretical, with full literature references; unfortunately now somewhat out of date.)

A. Pictet. The Vegetable Alkaloids, transl. by H. C. Biddle. New York, 1904. (Deals with questions of constitution and synthesis.)

E. Winterstein und G. Trier. Die Alkaloide, 1910. (Less detailed than the above or following; speculations on the mode of formation of alkaloids in plants; physiological action; includes the simpler amines, betaines, &c.)

J. Schmidt, in Abderhalden's Biochemisches Handlexicon, vol. v. pp. 1–452. Berlin, 1911. (Chiefly for literature references.)

E. Schmidt, Pharmazeutische Chemie, 1911, vol. ii. pp. 1541–1855. (Very complete; mentions many little-known alkaloids; unfortunately no literature references; deals most fully with official alkaloids.)

Allen's Commercial Organic Analysis, 1912, vol. vi. pp. 167–726, and 1913, vol. vii. pp. 1–94. (Full analytical and technical accounts of the better-known alkaloids.)

T. A. Henry. The Plant Alkaloids. London, 1913, pp. vi.–466. (The most complete general account in English.)

For questions of constitution and synthesis, the following monographs are useful:—

J. Schmidt. Ueber die Erforschung der Konstitution und die Versuche zur Synthese wichtiger Pflanzenalkaloide. Stuttgart, 1900; and the triennial supplements, Die Alkaloidchemie in den Jahren, 1900–1904, 1904–1907, 1907–1911. G. B. and F. L. P.

ALKANET. The Arabic name *Al-henne*, modified to *alkanna* or *al-kenna*, was originally applied to the lythraceous shrub *Lawsonia alba* (Lam.), the root of which was described as *Radix Alkannæ vera*, in contradistinction to the root of our alkanna, which is *Anchusa tinctoria* (Lam.), and which became known as *Radix Alkannæ spuria tinctoria*. The latter, or *False alkanet*, is also known as *Orcanette*, Fr.; *Orkanet*, Ger.; Languedoc bugloss or dyers' bugloss, *Radix Alkannæ spuria*. A rough plant with downy spear-shaped leaves, and clusters of purplish or reddish flowers; belongs to the *Boraginaceæ*. Found in Asia Minor, Greece, Hungary, &c. The roots, which have an astringent taste, occur in commerce, varying from the thickness of a quill to that of a finger.

Alkanet is one of the more ancient dyestuffs, having been employed by the Romans, but, on the other hand, it does not appear at any time to have attained such importance as madder, indigo, or even turmeric. The colouring matter of alkanet, known as *anchusin* or *alkannin*, has been examined by several chemists, but it is doubtful whether this compound has as yet been obtained in a chemically pure condition. Its composition is variously given as $C_{17}H_{10}O_4$ (Pelletier, Annalen, 6, 27), $C_{35}H_{20}O_8$ (Bolley and Wydlers, Annalen, 62, 41), $C_{15}H_{14}O_4$ (Carnelutti and Nasini, Ber. 13, 1514), and $C_{15}H_{14}O_4$ or $C_{15}H_{12}O_4$ (Liebermann and Römer, Ber. 20, 2428).

Alkannin forms a dark-red amorphous powder possessing a beetle-green iridescence, is readily soluble in most of the usual solvents, and its alkaline solution is deep-blue coloured. On distillation with zinc-dust it gives, according to Liebermann and Römer, both methylanthracene and anthracene.

Diacetylalkannin $C_{15}H_{12}O_4(C_2H_3O)_2$ forms a dull yellow micro-crystalline powder (C. and N.).

According to Eriksson (Ber. Deut. pharm. Ges. 1910, 20, 202), alkannin consists of two red pigments, the one being coloured green and the other blue by the action of alkalis. Red crystals have been observed by Tschirch in spaces in the cortex of old specimens of alkanet root. As alkannin is insoluble in water, in dyeing with alkanet an alcoholic extract is usually employed; and with aluminium and iron mordanted fabrics, violet and grey shades are respectively produced. These colours, however, are not fast to light, and are somewhat readily affected by weak alkalis or acids.

Haussmann of Mulhouse introduced alkanet into calico-printing, and for a short time it appears to have played a quite important part, but it is now little if at all employed in Europe for ordinary dyeing purposes. It is still used for colouring artificial wines, pomades, hair-oils, sweets, &c., and for these purposes it is well adapted on account of its ready solubility and harmless nature.

Böttger (J. pr. Chem. 107, 146) and Eng (Jahres. 70, 935) recommend the use of papers stained by alkanet as indicators in alkalimetry.

According to Jolin (Chem. Schriften über Alkanna, iv. 84), Thomson (Pharm. J. [3] 16, 860), and Eriksson (*l.c.*), alkanet root contains from 5 to 6 p.c. of anchusin. A. G. P.

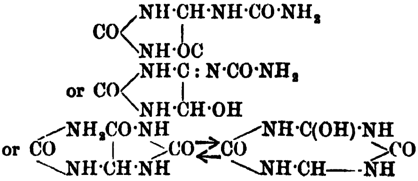
ALKANNA or **AL-KENNA.** The powdered root and leaves of the *Lawsonia alba* (Lam.), used in the East for dyeing the nails, teeth, hair, and garments. Used in Persia mixed with lime for dyeing the tails of horses.

ALKANNIN (ANCHUSIN) *v.* ALKANET.

ALKASAL *v.* SYNTHETIC DRUGS.

ALLANITE (*v.* ORTHITE). This is variously regarded as a synonym or as a variety of orthite. The original allanite was discovered at Kakarsuatsiak in east Greenland by C. L. Giesecke in 1806, described by T. Allen in 1808, and named by T. Thomson in 1810. Similar material has been found at numerous other localities in Greenland (O. B. Böggild, Mineralogia Groenlandica, Kjöbenhavn, 1905). L. J. S.

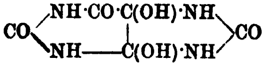
ALLANTOIN. *Glyoxyldiureide* $C_4H_6O_3N_4$



(Titherley, Chem. Soc. Trans. 1913, 103, 1336; Biltz, Ber. 1913, 46, 3410; Mendel and Dakin. Chem. Soc. Trans. 1915, 107, 434) was found originally in the allantoic liquid of cows (Vauquelin and Buniva, Ann. Chim. 23, 269; Lassaigne, Ann. Chim. Phys. [2] 17, 301) and in the urine of newly-born calves (Wöhler, Annalen, 70, 229); it occurs in the blood of the pig and ox (Hunter, J. Biol. Chem. 1917, 28, 369–374); in beetroot (Smokenski, Zeitsch. Ver Dtsch. Zuckerind, 1910, 1251); in root of *phaseolus multiflorus* (Power and Salway, Pharm. J. 1913, [4] 36, 552); in *Anabasis aretioides* and other plants (Stieger, Zeitsch. physiol. Chem. 1913, 86, 269; Johnson, J. Amer. Chem. Soc. 1914, 36, 1, 339); also in the young leaves, buds, and stem of the plane tree (*Platanus orientalis*); sycamore (*Acer pseudoplatanus*); in the bark of the horse-chestnut (*Æsculus hippocastanum*); in comfrey root (Titherley and Coppin, Pharm. J. 1912, 34, 92); and in rice polishings (Funk, J. of Physiol. 45, 75). Under normal conditions of growth 0·25 gram allantoïn may be isolated from 440 grams of fresh young leaves of the plane, but when the branches are cut in bud and the buds allowed to open in water, the amount of allantoïn increases to 0·5 or 1 p.c. of the dried leaves (Schulze and Barbieri, Ber. 1881, 14, 1602; J. pr. Chem. [2] 25, 145; Schulze and Bosshead, Zeitsch. physiol. Chem. 1884, 9, 420). It has been found in the nitrogenous constituents of wheat-germs (Richardson and Crampton, Ber. 1886, 19, 1180); in tobacco seeds (Scurti and Perciabosco, Gazz. chim. ital. 1906, 36, ii. 626); and in crude beet juice (v. Lippman, Ber. 1896, 29, 2652). Allantoïn is a normal constituent of the urine of mammals; the amount varies in different species, being greatest in the dog and least in man (Frerichs, Städeler, J. 1854, 7, 714; Wiechowski, Biochem.

Zeitsch. 1909, 19, 368; Schittenhelm, Zeitsch. physiol. Chem. 1909, 63, 248, 269, 283, 289). The whole quantity of allantoïn excreted by man on a milk and vegetable diet may be derived directly from the food (Ackroyd, Bio-Chem. J. 1911, 5, 400). In the case of the dog the amount of allantoïn in the urine is increased after a diet of animal food (Salkowski, Ber. 1878, 11, 500), of calf's thymus (Cohn. Zeitsch. physiol. Chem. 1898, 25, 507; Mendel, Amer. J. Physiol. 6, xiv.–xv.; M'Lachlan, Proc. Roy. Soc. Edin. 1906, 26, 95; and on increasing the ingestion of water per day from 900 to 3450 c.c. there is an increase of 20 p.c. in output (Fairhall and Hawk, J. Amer. Chem. Soc. 1912, 34, 546). There is about 30 p.c. increase in elimination of allantoïn if adrenaline is introduced (Falta, Zeitsch. exp. Path. Ther. 15, 356). It is also increased after the administration of uric acid (Salkowski, Ber. 1876, 9, 719; Swain, Amer. J. Physiol. 1910, 6, 38; Wiechowski, Beitr. Chem. Physiol. Path. 1908, 11, 109; Biochem. Zeitsch. 1910, 25, 431), or of nucleic acid (Mendel, *l.c.*; Schittenhelm, Zeitsch. physiol. Chem. 1910, 66, 53; Wiechowski, *l.c.*). Allantoïn is therefore to be regarded as an end-product of uric acid metabolism in the case of such animals as dogs and rabbits (Wiechowski, *l.c.*; Schittenhelm, *l.c.*). For the importance of allantoin as end-product in purine metabolism in monkeys, *see* Hunter and Giveus, Pro. Amer. Physiol. Soc. 1910, xv.–xvi.; Amer. J. Physiol. 27, 1910–1911, xv. Allantoïn is of therapeutic value (Funk, J. of Physiol. 45, 489–492), and is used to induce cell proliferation in cases of burns, &c. (Titherley and Coppin, Pharm. J. 1912 [iv.] 34, 92–94). Allantoïn injected increases the blood pressure (Backmann, Zentral. blatt f. Physiol. 26, 166).

The method of preparation of allantoïn by oxidising uric acid with lead peroxide in presence of water is due to Liebig and Wöhler (Annalen, 1838, 26, 245); it has been modified by Mulder (Annalen, 1871, 159, 349), who effects the oxidation in dilute acetic acid solution and in bright daylight; by this method 100 grams of uric acid yield 30–32 grams of allantoïn. A quantitative yield of allantoïn is obtained when uric acid is oxidised by an alkaline solution of potassium permanganate, and the intermediate compound



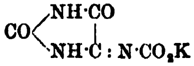
$$\mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH{\cdot}CO{\cdot}C(OH){\cdot}NH}\\ \mathrm{NH{-\!\!-\!\!-}C(OH){\cdot}NH}\end{array}\right\rangle\mathrm{CO}$$

decomposed by acetic acid (Sundvik, Zeitsch. physiol. Chem. 1904, 41, 343; Behrend, Annalen, 1904, 333, 141; and 1915, 410, 340–341). Allantoïn is also obtained by the action of nitrous acid on dialuric acid (Gibbs, Annalen Suppl. 1870, 7, 337). The synthesis of allantoïn has been effected (1) by Grimaux (Compt. rend. 1876, 83, 62) by heating a mixture of glyoxylic acid (1 part) and carbamide (2 parts) at 100° for 8–10 hours; (2) by Michael (Amer. Chem. J. 1883, 5, 198) by heating a mixture of mesoxalic acid and carbamide in equal proportions at 110°; (3) by Simon and Chavanne (Compt. rend. 1906, 143, 51) by the action of ammonia or alkali hydroxides on ethyl allantoate $CH(NH{\cdot}CO{\cdot}NH_2)_2CO_2Et$, obtained by the condensation of ethyl glyoxylate with carbamide; (4) by Behrend and Zieger (Annalen, 1915, 410, 337–373) by condensing uric acid and alloxanic acid in boiling acetic anhydride; (5) by Biltz and Giesler (Ber. 1913, 46, 3424) by the action of potassium cyanate on 5-amino hydantoïn hydrochloride; and (6) by Biltz and Heyn (Annalen, 1916, 413, 39) by the action of barium hydroxide solution on spiro-5,5,-dihydantoin.

Allantoïn is readily soluble in boiling water sparingly so in cold (1 : 131·5 at 21·8°) (Grimaux Ann. Chim. Phys. 1877, [v.] 11, 389); it is optically inactive (Mendel and Dakin, J. Biol. Chem. 1910, 7, 153); crystallises in glassy monoclinic prisms (Dauber, Annalen, 1849, 71, 511; Hunter, Biochem. J. 28, 369); its heat of combustion at constant pressure is +413·8 Cal. (*cf.* Emery, Benedict, Amer. J. Physiol. 28, 1911, 303), and heat of formation +170·4 Cal. (Matignon, Ann. Chim. Phys. 1893, [vi.] 28, 106). It melts at 227° (Titherley and Coppin), 235° with decomposition (Watt, Pharm. J. 1917, 45, 283), 235°–236° (decomp.) (Biltz and Heyn, *ibid.* 40); 232° (Hunter, *l.c.*).

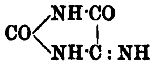
Allantoin forms a silver salt $C_4H_5O_3N_4Ag$ (Liebig and Wöhler, *l.c.*) and a potassium salt $C_4H_5O_3N_4K$ (Mulder, *l.c.*); it also combines with certain metallic oxides to form sparingly soluble compounds; the mercury, copper, zinc, lead, and cadmium derivatives are described by Limpricht (Annalen, 1853, 88, 94). (For the method of estimating allantoïn based on the sparing solubility of the silver and mercury derivatives, *see* Loewi, Zeitsch. anal. Chem. 1900, 39, 266; Poduschka, *ibid.* 267). Allantoïn from even 0·1 p.c. solution can be nearly quantitatively precipitated with mercuric chloride and sodium hydroxide or carbonate (Hunter, J. Biol. Chem. 1916, 28, 270). For titrimetric estimation in urine, *see* Handovsky (Zeitsch. physiol. Chem. 90, 211–220); for estimation in urine and in presence of sugar, Plimmer and Skelton (Biochem. J. 1914, 8, 70–73, and 641–648); Giveus (J. Biol. Chem. 1914, 18, 417–424).

Allantoïn is oxidised by potassium ferricyanide in the presence of potassium hydroxide to potassium allantoxanate



$$\mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}C:N{\cdot}CO_2K}\end{array}\right.$$

(van Embden, Annalen, 1873, 167, 39); the free acid does not exist, but breaks down, when liberated from its salts, into carbon dioxide and allantoxaïdin



$$\mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}C:NH}\end{array}\right.$$

(Ponomareff, Ber. 1878, 11, 2156). For oxidation of with bromine liquors (*see* Cordier, Monatsh. 33, 759–796). Methylallantoïn and isomerides (Fischer and Ach, Ber. 1899, 32, 2745; Biltz and Heyn, Annalen, 1916, 413, 83–85, and 97); 1-*methylallantoïn* (α-methylallantoïn) obtained from 9-methyl uric acid, has m.p. 250°–252° (decomp.), Fischer and Ach, m.p. 255°–259° (corr.) decomp.; 3-methyl allantoïn (β-*methylallantoïn*) crystallises in prisms with one molecule of water, m.p. 226°–227°, decomp., Fischer and Ach, m.p. 225°–227° (corr.) decomp.; 3, 8-*dimethylallantoïn* is obtained from 3, 7-dimethylspiro-dihydantoïn, m.p. 222°, turns yellow (decomp.); 1, 6-

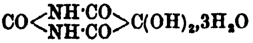
dimethylallantoïn, obtained from 1, 9-dimethylspirodihydantoin, m.p. 226°–227° (K. Th.) (decomp.). M. A. W.

ALLEMONITE. A native alloy of arsenic and antimony, $SbAs_3$, found at Allemont in the Dauphiné, Przibram in Bohemia; and Andreasberg in the Hartz.

ALLMATEIN. Trade name for a condensation product of hæmatoxylin and formaldehyde.

ALLOSAN. Trade name for santalyl allophanate.

ALLOXAN. Mesoxalylcarbamide

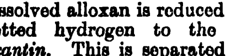


$$CO{<}\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}{>}C(OH)_2,3H_2O$$

found by Liebig (Annalen, 121, 81) and by Lang (Zeitsch. anal. Chem. 6, 294) in certain pathological excrétions, is one of the oxidation products of uric acid, and was first prepared by Brugnatelli (Ann. Chim. Phys. 1817, 8, 201; from Giornale di Fisica, decade seconde i. 117), under the name of *erythric acid*, by oxidising uric acid by means of nitric acid, chlorine or iodine. Liebig and Wohler (Annalen, 1838, 26, 256), who systematically studied the oxidation of uric acid, gave to this product the name of *alloxan*, regarding it as bearing the same relation to *allantoin* and *oxalic acid* that *oxaluric acid* does to *oxalic acid* and *urea*. According to Liebig and Wöhler (*l.c.*) and to Gregory (Mem. Chem. Soc. 1848, iii. 44), alloxan can be obtained most readily and with a yield of 90 p.c. by careful oxidation of uric acid by means of nitric acid, sp.gr. 1·412.

According to Schlieper (Annalen, 1845, 55, 261), the oxidation of uric acid to alloxan is more conveniently effected with hydrochloric acid and potassium chlorate; 4 parts of uric acid are mixed with 8 parts of hydrochloric acid, and 1 part of finely powdered potassium chlorate added in successive small quantities, avoiding the liberation of chlorine; after two or three hours the dissolved alloxan is reduced by means of sulphuretted hydrogen to the sparingly soluble *alloxantin*. This is separated from the sulphur by crystallisation from hot water, and oxidised to alloxan by the action of diluted nitric acid. Biltz (Annalen, 1916, 413, 60) prepares alloxan from uric acid in one operation by oxidation with chlorine.

Alloxan crystallises from warm saturated aqueous solution in large triclinic prisms containing $4H_2O$; on exposure to the air or on heating at 100° it loses $3H_2O$, and the dried compound has the composition expressed by the formula



$$CO{<}\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}{>}C(OH)_2$$

(Lang, Grailich, J. 1858, 308; Hartley, Chem. Soc. Trans. 1905, 87, 1802); it is also obtained in oblique rhombic prisms, belonging to the monoclinic system on evaporating an aqueous solution at 65°–70°. The remaining molecule of water is lost at 150°. By heating under reduced pressure it is possible to dehydrate alloxan and its mono- and dimethyl derivaties, all of which sublime unchanged in vacuum.

Alloxan anhydride $C_4H_2O_4NO_2$, yellow rhombic crystals, has m.p. 256° (decomp.).

They are deposited from alcohols containing a little hydrochloric acid in the form of alcoholates; these when heated eliminate the molecule of alcohol and leave a residue with the melting-point of the anhydride (Biltz, Ber. 1912, 45, 3659–3675).

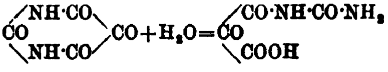
Alloxan anhydride $C_4H_2O_4N_2$, yellow rhombic crystals, has m.p. 256° (decomp.).

When crystals of alloxan are kept for some years in closed vessels they sometimes undergo spontaneous decomposition, forming alloxantin, parabanic acid, and carbon dioxide. According to Gregory (Annalen, 1853, 87, 126), this is due to the presence of traces of nitric acid contained in the water of crystallisation. Similar phenomena were observed by Baumert (Pogg. Ann. 1860, 110, 93), by Heintz (Pogg. Ann. 1860, 111, 436), and by Otto (Annalen Suppl. 1865, 4, 256). Cases of spontaneous explosive decomposition of alloxan are recorded by Wheeler and by Bogert (J. Amer. Chem. Soc. 1910, 32, 809); the products of decomposition being carbon dioxide, carbamide, oxalic acid, and alloxantin (Gortner, J. Amer. Chem. Soc. 1911, 33, 85).

The molecular heat of combustion of alloxan is 276·5 Cal. (Matignon, Ann. Chem. Phys. 1893, [vi.] 28, 300); the dissociation constant is $2{\cdot}32\times10^{-7}$ (Wood, Chem. Soc. Trans. 1906, 89, 1835). The dissociation constant K (in diazoacetic ester solution) $=0{\cdot}03542$, $C_H=0{\cdot}000920$, and the sp. conductivity at 25° (not deducting that of water, $1{\cdot}1\times10^{-5}=1{\cdot}27\times10^{-5}$ (Calcagin, Atti R. Accad. dei Lincei, [5] 25, i. 643–648). In common with the other simple ureides, alloxan shows no absorption bands in its spectrum (Hartley, Chem. Soc. Trans. 1905, 87, 1815).

Alloxan is readily soluble in alcohol or water; the solution is acid to litmus, stains the skin purple, and imparts to it a curious and unpleasant odour. In its physiological action alloxan affects the central nervous system, producing first stimulation, then paralysis. When taken internally it is excreted in the urine as alloxantin and parabanic acid (Lusini, Chem. Zentr. 1895, ii. 311, 727, 838; Koehne, Chem. Zentr. 1894, ii. 296).

Alloxan is readily oxidised by warm dilute nitric acid, forming carbon dioxide and *parabanic acid* (*oxalylcarbamide*) (*q.v.*); is reduced by sulphuretted hydrogen, stannous chloride, zinc, and hydrochloric acid, or by boiling with excess of sulphurous acid to *alloxantin* (*q.v.*); and is readily hydrolysed by alkali carbonates or by the hydroxides or chlorides of the alkaline earths, forming the corresponding salt of *alloxanic acid*. The barium and calcium salts are insoluble.



$$CO{<}\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}{>}CO+H_2O=CO{<}\genfrac{}{}{0pt}{}{CO\cdot NH\cdot CO\cdot NH_2}{COOH}$$

If, however, excess of alkali is employed or the solutions are heated, the hydrolysis is carried to completion with the formation of mesoxalic acid and carbamide (Schlieper, Annalen, 1845, 55, 263; 56, 1; Biltz, Annalen, 1916, 413, 70). Alloxan gives a deep-blue colour with ferrous salts, but no precipitate is formed unless an alkali is present. According to Agrestini (Boll. Chim. Farm. 1902, 41, 5–7; Chem. Zentr. 1902, i. 631), the formation of blue colour is dependent on the presence of a trace of ammonia or caustic alkali, and the same deep-blue colour is also given by *pure* ferric salts under similar conditions. For similarity in the behaviour of triketohydrindene hydrate and alloxan, see Ruhemann (Chem. Soc. Trans. 1911, 99, 793); Traube (Ber. 1911, 44, 3145); Retinger (J. Amer. Chem. Soc. 1917, 39, 1059). Alloxan gives the murexide reaction, and Angrestini (*l.c.*) finds that the ammonia in the reaction can be replaced by certain acid amides, amino acids, or substituted amines; Rosenheim's alloxan test for choline (J. Physiol. 1905, 33, 220), namely, the formation of a deep red-violet colour when a drop of a 1 p.c. solution of choline hydrochloride is evaporated on the water-bath with a few drops of a saturated solution of alloxan, is probably a reaction of the same order.

Other tests for alloxan are (1) the formation of a deep violet-blue colour when a solution of alloxan is boiled for a few minutes with a drop of pyrrole. The colour changes to red on cooling, becoming green and then intensely blue on the addition of alkali. (2) The blue-green solution obtained on mixing concentrated sulphuric acid solutions of alloxan (or alloxantin) and pyrocatechol, the colour changes to an intense green on dilution (Agrestini, *l.c.*). Hartley (Chem. Soc. Trans. 1905, 87, 1816) finds that hydrated alloxan, when powdered along with pure calcite, acquires a yellowish-pink tinge. After half an hour the colour is decided and it is permanent; on adding water a red solution is obtained. When alloxan, dried at 100°, is similarly treated, there is no colour developed until water has been added. Alloxanic acid gives no such colour reaction. Alloxan yields alcoholates, phenolates, and sulphites (Biltz, Ber. 1912, 45, 3667–3670), also a compound with hydrogen peroxide $(C_4H_2O_4N_2)_{10}H_2O_2$ (Stolzenberg, Ber. 1916, 49, 1545).

For other derivatives of alloxan, *see* Behrend and Zieger (Annalen, 1915, 410, 337–373).

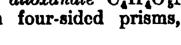
Potassium alloxan $C_4H_3O_5N_2K$, pale red needles, decomposes about 235°.

Carbamide alloxanate $C_4H_4O_5N_2,CO(NH_2)_2$, crystallises in four-sided prisms, decomposes 155°–156°.

Urea and alloxan also form a compound $C_5H_6O_6N_4$, decomposes 117° or 133°–134°, is probably a salt-like compound. It gives uric acid and glycol when heated; boiled with acetic anhydride it yields an anhydride $C_5H_6O_5N_4$, microscopic needles, m.p. 185°–186°.

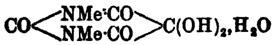
Methyl alloxanate $C_5H_6O_5N_2$, prisms, decomposes 175°–176°.

The following *homologues* of alloxan have been described:—*Methylalloxan*



$$\mathrm{CO}\left<\begin{matrix}\mathrm{NMe\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\right>\mathrm{CO}$$

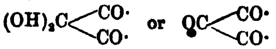
prepared from methyl uric acid (Hill, Ber. 1876, 9, 1092); from ζ-uric acid (Fischer, Ber. 1899, 32, 2731); from theobromine (Maly, Andreasch, Monatsh. 1882, 3, 108; Fischer and Clemm, Ber. 1897, 30, 3090). It crystallises from water in brilliant colourless prisms, becomes anhydrous at 60° in a vacuum, and decomposes at 156°. *Dimethylalloxan*



$$\mathrm{CO}\left<\begin{matrix}\mathrm{NMe\cdot CO}\\ \mathrm{NMe\cdot CO}\end{matrix}\right>\mathrm{C(OH)_2,H_2O}$$

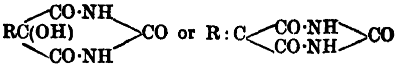
prepared by oxidising caffeine (Fischer, Annalen, 1882, 215, 257; Maly, Andreasch, Monatsh. 1882, 3, 96), by boiling dichlorodimethylbarbituric acid with water or silver oxide (Techow, Ber. 1894, 27, 3083), loses $1H_2O$ when dried over sulphuric acid, decomposes at 100°; the anhydrous compound is a pale yellow powder soluble in alcohol and has m.p. 252°–255° (decomp.) (Biltz, Ber. 1912, 45, 3659). *Diethylalloxan* $C_8H_{10}O_4N_2$, prepared by oxidising 1:3-diethylbarbituric acid with nitric acid, containing a little nitrous acid (Sembritzki, Ber. 1897, 30, 1820). *Methylethylalloxan*, from ethyltheobromine by oxidation (Pommerehne, Apoth. Zeit. 1897, 12, 5). Some derivatives of 1:3-diphenylalloxan have been described by Whiteley (Chem. Soc. Trans. 1907, 91, 1344).

Inasmuch as the alloxan molecule contains the mesoxalyl radical



$$\mathrm{(OH)_2C}\left<\begin{matrix}\mathrm{CO\cdot}\\ \mathrm{CO\cdot}\end{matrix}\right. \quad \text{or} \quad \mathrm{OC}\left<\begin{matrix}\mathrm{CO\cdot}\\ \mathrm{CO\cdot}\end{matrix}\right.$$

it forms a wide series of condensation products through the medium of the :C(OH)₂ or :CO group yielding derivatives of the type

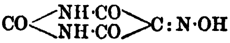


$$\mathrm{RC(OH)}\left<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}\right>\mathrm{CO} \quad \text{or} \quad \mathrm{R:C}\left<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}\right>\mathrm{CO}$$

respectively. These compounds will be described under the following eight headings.

1. Condensation of Alloxan with Bisulphites.—Alloxan forms condensation products of the type $C_4H_2N_2O_4,NaHSO_3,1\frac{1}{2}H_2O$ with alkali bisulphites (Limpricht and Wuth, Annalen, 1858, 108, 41), and with the sulphites of certain organic bases (Pellizzari, Annalen, 1888, 248, 146). *Alloxan ethylamine sulphite* $C_2H_7N\cdot SO_3H_2\cdot C_4H_2N_2O_4,H_2O$; *Alloxan aniline sulphite* $C_6H_7N\cdot SO_3H_2,C_4H_2N_2O_4,2H_2O$; *Alloxan methylaniline sulphite* $C_7H_9N\cdot SO_3H_2,C_4H_2N_2O_4\cdot 2H_2O$; *Alloxan dimethylanilinesulphite* $C_8H_{11}N\cdot SO_3H_2,C_4H_2N_2O_4,4H_2O$, are described and the crystallographic constants are given. The *benzidine* compound contains $1H_2O$; *toluidine, aminobenzoic acid,* and *aspartic acid* yield similar compounds. *Alloxan pyridine sulphite* is triclinic, and anhydrous crystalline derivatives are afforded by *quinoline, picoline, morphine,* and *cinchonine*; the *strychnine* compound has $1H_2O$, and the *brucine* compound $1\frac{1}{2}H_2O$.

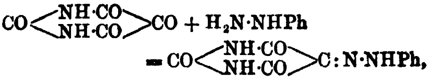
2. Condensation of Alloxan with Hydroxylamine.—Alloxan condenses with hydroxylamine hydrochloride (Ceresole, Ber. 1883, 16, 1133) to form the *oxime, violuric acid*



$$\mathrm{CO}\left<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\right>\mathrm{C:N\cdot OH}$$

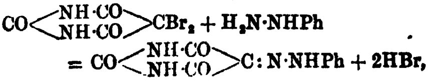
(*q.v.*).

3. Condensation of Alloxan with Hydrazines.—Hydrazones of alloxan and its homologues can be prepared by the condensation of (*a*) the alloxan with the hydrazine



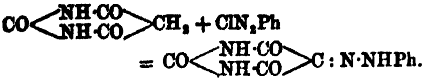
$$\mathrm{CO}\left<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\right>\mathrm{CO} + \mathrm{H_2N\cdot NHPh} = \mathrm{CO}\left<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\right>\mathrm{C:N\cdot NHPh},$$

(*b*) the dibromo- derivative of the corresponding barbituric acid with the hydrazine



$$\mathrm{CO}\left<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\right>\mathrm{CBr_2} + \mathrm{H_2N\cdot NHPh} = \mathrm{CO}\left<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\right>\mathrm{C:N\cdot NHPh} + \mathrm{2HBr},$$

(*c*) the corresponding barbituric acid with the diazonium chloride



$$\mathrm{CO{<}\begin{smallmatrix}NH\cdot CO\\ NH\cdot CO\end{smallmatrix}{>}CH_2 + ClN_2Ph = CO{<}\begin{smallmatrix}NH\cdot CO\\ NH\cdot CO\end{smallmatrix}{>}C : N\cdot NHPh.}$$

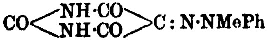
And the following hydrazones have been prepared by one or more of these methods:—*Alloxanphenylhydrazone*

$$\mathrm{CO{<}\begin{smallmatrix}NH\cdot CO\\ NH\cdot CO\end{smallmatrix}{>}C : N\cdot NHPh}$$

pale-yellow crystals, melts and decomposes at 298°–300°; 1 : 3-*Dimethylalloxanphenylhydrazone*

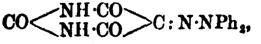
$$\mathrm{CO{<}\begin{smallmatrix}NMe\cdot CO\\ NMe\cdot CO\end{smallmatrix}{>}C : N\cdot NHPh}$$

slender yellow crystals, m.p. 261° the *o*- and *p*-nitro derivatives are yellow crystalline substances and decompose at 310° and 300° respectively (Kühling, Ber. 1891, 24, 4140; 1898, 31, 1972); *alloxanphenylmethylhydrazone*



$$\mathrm{CO{<}\begin{smallmatrix}NH\cdot CO\\ NH\cdot CO\end{smallmatrix}{>}C : N\cdot NMePh}$$

brick-red hexagonal plates, decomposes at 189°–191° (Whiteley, Chem. Soc. Proc. 1906, 22, 201); *alloxandiphenylhydrazone*



$$\mathrm{CO{<}\begin{smallmatrix}NH\cdot CO\\ NH\cdot CO\end{smallmatrix}{>}C : N\cdot NPh_2,}$$

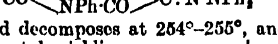
bright-yellow powder, melts above 270° (Armstrong and Robertson, Chem. Soc. Trans. 1905, 87, 1291); 1 : 3-*diphenylalloxanphenylhydrazone*

$$\mathrm{CO{<}\begin{smallmatrix}NPh\cdot CO\\ NPh\cdot CO\end{smallmatrix}{>}C : N\cdot NHPh}$$

bright-yellow needles that decompose at 265°, the *p-nitro* derivative forms yellow prisms with a purple reflex and melt and decompose at 274°; 1 : 3-*diphenylalloxanphenylmethylhydrazone*

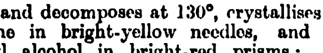
$$\mathrm{CO{<}\begin{smallmatrix}NPh\cdot CO\\ NPh\cdot CO\end{smallmatrix}{>}C : N\cdot NMePh}$$

decomposes at 175° and crystallises in orange red prisms or bright-yellow needles; 1 : 3-*diphenylalloxandiphenylhydrazone*



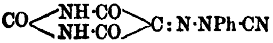
$$\mathrm{CO{<}\begin{smallmatrix}NPh\cdot CO\\ NPh\cdot CO\end{smallmatrix}{>}C : N\cdot NPh_2}$$

melts and decomposes at 254°–255°, and forms yellow crystals yielding an orange-red powder on trituration; 1 : 3-*diphenylalloxanphenylbenzylhydrazone*



$$\mathrm{CO{<}\begin{smallmatrix}NPh\cdot CO\\ NPh\cdot CO\end{smallmatrix}{>}C : N\cdot NPh\cdot CH_2Ph}$$

melts and decomposes at 130°, crystallises from benzene in bright-yellow needles, and from methyl alcohol in bright-red prisms; from toluene a mixture of the red prisms and yellow needles is obtained (Whiteley, Chem. Soc. Trans. 1907, 91, 1344); *alloxancyanophenylhydrazone*

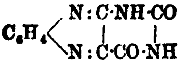


$$\mathrm{CO{<}\begin{smallmatrix}NH\cdot CO\\ NH\cdot CO\end{smallmatrix}{>}C : N\cdot NPh\cdot CN}$$

from alloxan and aminophenylcyanamide, straw-yellow compound, m.p. 286° (Rolla, Gazz. chim. ital. 1907, 37, i. 623).

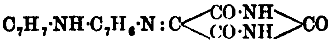
4. Condensation of Alloxan with Semicarbazide.—This reaction has been studied by Bromberg (Ber. 1897, 30, 131). He describes the compounds *alloxansemicarbazide* $C_5H_9O_6N_5$ and *dimethylalloxansemicarbazide* $C_7H_{11}O_5N_5$, but was not successful in determining their constitution.

5. Condensation of Alloxan with Diamines.—In the condensation of alloxan with *o*-diamines the ketonic carbonyl and one of the adjacent carbimido- groups take part, and the product is an *azine*; *alloxazine*



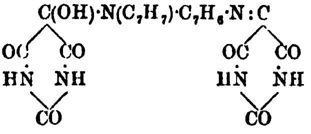
obtained from *o*-phenylenediamine, forms yellow microscopic crystals that decompose above 300°; similar derivatives were obtained from 3 : 4-diaminotoluene and *a*-β-diaminonaphthalene (Kühling, Ber. 1891, 24, 2363); for the effect of oxidising and reducing agents on these compounds, compare Kühling, Ber. 1895, 28, 1968; 1899, 32, 1650).

The condensation of alloxan with monosubstituted *o*-diamines results in the formation of two compounds according as one or more alloxan molecules take part in the reaction. Thus alloxan condenses with *orthaminoditolylamine* at the ordinary temperature to form *alloxanylorthaminoditolylamine*



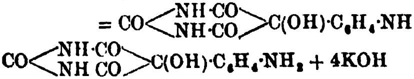
$$\mathrm{C_7H_7\cdot NH\cdot C_7H_6\cdot N : C{<}\begin{smallmatrix}CO\cdot NH\\ CO\cdot NH\end{smallmatrix}{>}CO}$$

glittering yellow prisms, that melt and decompose at 252°, and dissolve in concentrated sulphuric acid with a deep red colour; if, however, the condensation is effected in the presence of fuming hydrochloric acid and the mixture is boiled, *dialloxanylorthaminoditolylamine*

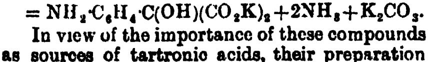


is formed. It is crystalline, and blackens at 300°, dissolves readily in alkali carbonates, and gives a deep-blue solution in concentrated sulphuric acid. Dimethylalloxan gives similar derivatives (Kühling, Ber. 1893, 26, 540), and similar condensation products are obtained from alloxan and phenyl-*o*-phenylenediamine, *o*-aminodi-*p*-tolylamine, and N-methyl-*o*-phenylenediamine (Kühling and Kaselitz, Ber. 1906; 39, 1314); and from tetramethyl-*m*-phenylenediamine (Sachs and Appenzeller, Ber. 1908, 41, 91).

6. Condensation of Alloxan with Aromatic amines.—Alloxan condenses readily with primary aromatic amines (Pellizzari, Gazz. chim. ital. 1895, 17, 419) to form aminoaryl substituted dialuric acids, yielding on hydrolysis with alkali, the corresponding tartronic acid (*q.v.*). Thus aniline and alloxan give *p*-aminophenyldialuric acid, and this on hydrolysis yields *p*-aminophenyltartronic acid



$$\mathrm{CO{<}\begin{smallmatrix}NH\cdot CO\\ NH\cdot CO\end{smallmatrix}{>}C(OH)_2 + C_6H_5\cdot NH_2 = CO{<}\begin{smallmatrix}NH\cdot CO\\ NH\cdot CO\end{smallmatrix}{>}C(OH)\cdot C_6H_4\cdot NH_2.}$$



$$\mathrm{CO{<}\begin{smallmatrix}NH\cdot CO\\ NH\ CO\end{smallmatrix}{>}C(OH)\cdot C_6H_4\cdot NH_2 + 4KOH = NH_2\cdot C_6H_4\cdot C(OH)(CO_2K)_2 + 2NH_3 + K_2CO_3.}$$

In view of the importance of these compounds as sources of tartronic acids, their preparation forms the subject of a patent, D. R. P. 112174 (Frdl. 1900–1902, 158–159), in which the amino-aryl- dialuric and tartronic acids obtained from

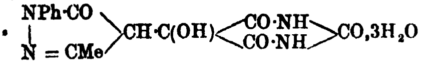
the following bases are described: ethylaniline, diethylaniline, benzylaniline, methylbenzylaniline, ethylbenzylaniline, diphenylamine, *p*-toluidine, *o*-ethyltoluidine, *o*-anisidine, methyl-*o*-anisidine, *o*-phenetidine, *m*-chloraniline, *m*-chlordimethylaniline, and *m*-chlordiethylaniline.

By careful oxidation with potassium permanganate of the alkali salts of the tartronic acids, or by oxidising the corresponding dialuric acid with mercuric oxide in presence of potassium hydroxide, the corresponding glyoxylic acid (*q.v.*) can be obtained

$$NH_2{\cdot}C_6H_4{\cdot}C(OH)(CO_2H)_2 + O = NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H + CO_2 + H_2O$$

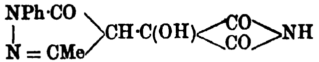
and the preparation by these methods of an important series of glyoxylic acids forms the subject of patents D. R. P. 117021, 26/11, 1900; and 117168, 3/12, 1900.

Alloxan condenses also with pyrazolone bases to form derivatives of dialuric acid (tartronylcarbamide), and these on hydrolysis with cold caustic alkali yield the corresponding substituted tartronimides (Pellizzari, Gazz. chim. ital. 1888, 18, 340). Thus *phenylmethylpyrazolonetartronyl carbamide*



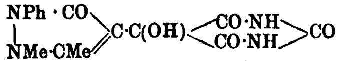
$$\begin{matrix}NPh{\cdot}CO\\ |\\ N=CMe\end{matrix}\!\!>CH{\cdot}C(OH)\!<\!\begin{matrix}CO{\cdot}NH\\ CO{\cdot}NH\end{matrix}\!>CO,3H_2O$$

forms long yellow needles that decompose at 170°–178°, and yield *phenylmethylpyrazolonetartronimide*



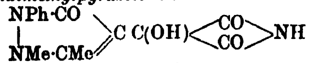
$$\begin{matrix}NPh{\cdot}CO\\ |\\ N=CMe\end{matrix}\!\!>CH{\cdot}C(OH)\!<\!\begin{matrix}CO\\ CO\end{matrix}\!>NH$$

on hydrolysis; *phenyldimethylpyrazolonetartronylcarbamide*



$$\begin{matrix}NPh{\cdot}CO\\ |\\ NMe{\cdot}CMe\end{matrix}\!\!>C{\cdot}C(OH)\!<\!\begin{matrix}CO{\cdot}NH\\ CO{\cdot}NH\end{matrix}\!>CO$$

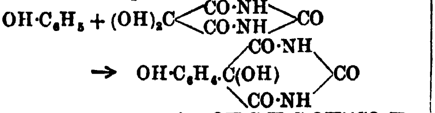
melts and decomposes at 261°, and yields *phenyldimethylpyrazolonetartronimide*



$$\begin{matrix}NPh{\cdot}CO\\ |\\ NMe{\cdot}CMe\end{matrix}\!\!>C{\cdot}C(OH)\!<\!\begin{matrix}CO\\ CO\end{matrix}\!>NH$$

decomposing at 245°–250°.

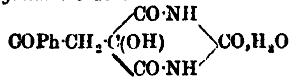
7. **Condensation of Alloxan with Phenols.**—Alloxan condenses in the presence of hydrogen chloride, sulphuric acid, or zinc chloride with mono- or polyhydroxy- phenols to form derivatives of dialuric acid (tartronylcarbamide), that promise to be of value for pharmaceutical purposes, and are readily converted by hydrolysis into the corresponding tartronic acid:



$$OH{\cdot}C_6H_5 + (OH)_2C\!<\!\begin{matrix}CO{\cdot}NH\\ CO{\cdot}NH\end{matrix}\!>CO \rightarrow OH{\cdot}C_6H_4{\cdot}C(OH)\!<\!\begin{matrix}CO{\cdot}NH\\ CO{\cdot}NH\end{matrix}\!>CO \rightarrow OH{\cdot}C_6H_4C(OH)(CO_2H)_2.$$

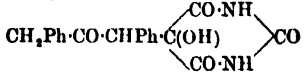
A description of the compounds obtained from alloxan and the phenolic compounds, phenol, *m*-cresol, *p*-cresol, guaiacol, pyrocatechol, resorcinol, hydroquinone, pyrogallol, *a*-naphthol, is given in D. R. P. 107720, 25/8, 1898; 113722, 9/7, 1900; 114904, 17/9, 1900; and the tartronic acids derived from them are described in D. R. P. 115817, 8/10, 1900.

8. **Condensation of Alloxan with Ketones.**—Alloxan condenses with acetophenone and certain of its homologues to form phenacyldialuric acid or its derivatives of which the following are described by Kühling (Ber. 1905, 38, 3003). Kühling and Schneider (Ber. 1909, 42, 1285): *phenacyldialuric acid*



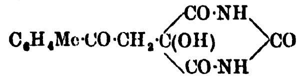
$$COPh{\cdot}CH_2{\cdot}C(OH)\!<\!\begin{matrix}CO{\cdot}NH\\ CO{\cdot}NH\end{matrix}\!>CO,H_2O$$

m.p. 212°, with decomposition; the *bromo-derivative* decomposes at 217°; *p-ethoxyphenacyldialuric acid* $C_{14}H_{14}O_6N_2$, m.p. 214°; the *bromo-* derivative, decomposes at 201°; *aγ-diphenylacetonyldialuric acid*



$$CH_2Ph{\cdot}CO{\cdot}CHPh{\cdot}C(OH)\!<\!\begin{matrix}CO{\cdot}NH\\ CO{\cdot}NH\end{matrix}\!>CO$$

m.p. 233° with decomposition; *p-methylphenacyldialuric acid*



$$C_6H_4Me{\cdot}CO{\cdot}CH_2{\cdot}C(OH)\!<\!\begin{matrix}CO{\cdot}NH\\ CO{\cdot}NH\end{matrix}\!>CO$$

m.p. 241°–242°, with decomposition; the *acetyl* derivative decomposes at 220°, the *benzoyl* at 215°; *p-methoxyphenacyldialuric acid* $C_{13}H_{12}O_6N_2$ decomposes at 227°, and yields an *acetyl* derivative, m.p. 207°.

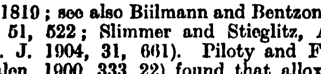
For condensation products of alloxan and substituted rhodamic acids (*see* Butscher, Monatsh. 1911, 32, 9–19), and alloxan with amino-antipyrine (*see* Meyer, Compt. rend. 1911, 152, 1677).

M. A. W.

ALLOXANIC ACID *v.* ALLOXAN; and Biltz, Heyn, Bergius (Annalen, 1916, 413, 368); Behrend and Zieger (Annalen, 1915, 410, 337).

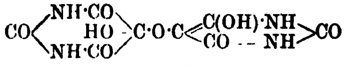
ALLOXANTIN $C_8H_6O_8N_4,2H_2O$ (Ritthausen, Ber. 1896, 29, 892) exists in small quantities in crude beet-juice (Lippmann, Ber. 1896, 29, 2645), and forms 34 to 36 p.c. of the products when *convicin* from sow-beans (*Vicia faba minor*) or from vetches (*Vicia sativa*) is hydrolysed by dilute mineral acids (Ritthausen, *l.c.*; J. pr. Chem. 1899, [ii.] 59, 487). Johnson (J. Amer. Chem. Soc. 1914, 36, 337–343) discusses its origin in plants. Alloxantin was first prepared by Liebig and Wöhler (Annalen, 1838, 26, 262) by oxidising uric acid with dilute nitric acid; or by the direct union of alloxan and dialuric acid, or by reducing a cold aqueous solution of alloxan with sulphuretted hydrogen or stannous chloride. According to Vitali (Chem. Zentr. 1898, i. 665, from Boll. Chim. Farm. 37, 65), the reduction can also be effected by means of hydriodic acid. Alloxantin was synthesised by Grimaux (Compt. rend. 1878, 87, 752) by heating malonic acid, carbamide and phosphoryl chloride at 150°, and passing sulphuretted hydrogen through a nitric acid solution of the crude product; or by passing sulphuretted hydrogen through a hot aqueous solution of dibromobarbituric acid (Compt. rend. 1879, 88, 86). Koech (Annalen, 1901, 315, 246) describes the conversion of *iso*dialuric acid into alloxantin by heating it with guanidine and acetic acid; the change seems to be due to the transformation of the *iso*dialuric acid into dialuric acid by the action of the base, and the subsequent oxidation of the dialuric acid to alloxantin, since, if the reaction is conducted in an atmosphere of carbon dioxide, dialuric acid only is obtained. An aqueous suspension of alloxantin possesses considerable oxygen consuming power (Thunberg, Skand. Arch. Physiol. 1916, 33, 217).

Alloxantin crystallises from aqueous solutions in small sharp rhombic prisms, containing 2 mols. H_2O; it becomes anhydrous after heating for 1-1½ hours at 150°, or for 5 hours at 107°–110°; it decomposes at 170° into hydurilic acid, ammonia, carbon monoxide, carbon dioxide, and oxalic acid; *turns* yellow at 225°, and decomposes at 253°–255° (Biltz, Ber. 1912, 45, 3675). It is decomposed into barbituric acid and parabanic acid when heated with concentrated sulphuric acid at 120°, or into allituric acid $C_6H_6O_4N_4$ when boiled with excess of hydrochloric acid (Schlieper, Annalen, 1845, 56, 20). Alloxantin is sparingly soluble in cold water (0·2885 gram per 100 c.c. at 25°, of which about 22 p.c. is undissociated, Biilman and Bentzon, Ber. 1918, 51, 522), yielding an acid solution that reduces solutions of silver salts, and gives a characteristic violet-blue precipitate with baryta water, changing on warming into the colourless barium alloxanate which undergoes further decomposition into barium mesoxalate and barium carbonate (Liebig and Wöhler, Annalen, 1838, 26, 312). Alloxantin has a molecular heat of combustion = 584·7 Cals. (Matignon, Ann. Chim. Phys. 1893, [6] 28, 323), and a freshly prepared aqueous solution shows a remarkable absorption band in the ultraviolet, which disappears upon keeping the solution, owing to the decomposition of the alloxantin into alloxan and dialuric acid (Hartley, Chem. Soc. Trans. 1905, 87, 1814). For this reason Hartley expresses the constitution of alloxantin by the formula



$$CO\left<\begin{matrix}NH\cdot CO\\ HO-\\ NH\cdot CO\end{matrix}\right>C\cdot O\cdot C\left<\begin{matrix}CO\cdot NH\\ -H\\ CO\cdot NH\end{matrix}\right>CO$$

(*ibid.* 1810; see also Biilmann and Bentzon, Ber. 1918, 51, 522; Slimmer and Stieglitz, Amer. Chem. J. 1904, 31, 661). Piloty and Finckh (Annalen, 1900, 333, 22) found that alloxantin was resolved into alloxan and dimethylamine dialurate, by boiling with dimethylamine acetate, and suggest the constitutional formula



$$CO\left<\begin{matrix}NH\cdot CO\\ HO-\\ NH\cdot CO\end{matrix}\right>C\cdot O\cdot C\left<\begin{matrix}C(OH)\cdot NH\\ CO\ --\ NH\end{matrix}\right>CO$$

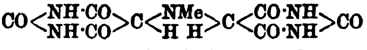
in which the relationship between alloxantin and alloxan is the same as that existing between quinhydrone and quinone. In diazo acetic ester the dissociation constant is 0·0000331, concentration of H ions 0·00001644, and sp. conductivity at 25° (not deducting that of water $1,1\times10^{-6}$) $1,13\times10^{-5}$ (Calcagni, Atti. R. Accad. dei Lincei. [5] 25, i. 643; *see* also Richter, Ber. 1911, 44, 2155; Johnson, J. Amer. Chem. Soc. 1914, 36, 337).

Alloxantin is readily converted into murexide (*q.v.*) by the action of ammonia, into alloxan by mild oxidising agents, and into dialuric acid by reducing agents. In its physiological action alloxantin resembles alloxan, but is especially poisonous to cold-blooded animals, the blood showing strong reducing properties; when taken internally it appears in the urine as parabanic acid, and in smaller quantities as dialuric acid, murexide, and alloxantin itself (Kowalewski, Chem. Zentr. 1887, 1296; Susini, Ann. Chim. Farm. 1895, 21, 241; 1896, 22, 341, 385).

Acetylalloxantin $C_{10}H_8O_9N_4,H_2O$, obtained by the interaction of acetyl dialuric acid and alloxan, crystallises in thin leaflets, becomes anhydrous when kept in a vacuum over sulphuric acid, melts and decomposes at 263°–265°, and is slowly hydrolysed by hot water with the formation of alloxantin.

Benzoylalloxantin $C_{15}H_{10}O_9N_4,H_2O$, similarly formed from benzoyl dialuric acid and alloxan, crystallises in colourless six-sided plates, and melts at 253°–255° (Behrend and Friedrich, Annalen, 1906, 344, 1).

Alloxantin is decomposed when boiled in an aqueous solution of the hydrochloride of a primary amine, yielding alloxan, together with the corresponding *dibarbiturylalkylamine*. These are colourless crystalline dibasic acids, hydrolysed by boiling with aqueous alkali hydroxides into dialuric acid and the amine. *Dibarbiturylmethylamine*



$$CO<\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}>C<\begin{matrix}NMe\\ H\quad H\end{matrix}>C<\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}>CO$$

decomposes at 280°, *dibarbiturylethylamine* decomposes at 235°, *dibarbiturylphenylamine* becomes blue at 240°, *dibarbituryl-α-naphthylamine* becomes black at 260°, the corresponding β-compound decomposes at 260°, and *dibarbiturylcarbamide* $CO(NH\cdot C_4H_3O_3N_2)_2$ decomposes above 300°.

The following homologues of alloxantin have been prepared: *methylalloxantin* $C_9H_8O_8N_4,3H_2O$ from methylalloxan and dialuric acid (Andreasch, Monatsh. 1882, 3, 431); sym-*dimethylalloxantin* $C_{10}H_{10}O_8N_4,4H_2O$ from methylalloxan (Maly, Andreasch, Monatsh. 1882, 3, 109), unsym-*dimethylalloxantin* $C_{10}H_{10}O_8N_4,H_2O$ from dimethyldialuric acid and alloxan (Andreasch, Monatsh. 1882, 3, 428). *Tetramethylalloxantin* $C_{12}H_{14}O_8N_4$ *amalic* acid (from ἁμαλός = soft, so called on account of its feebly acid reaction), prepared (1) by oxidising caffeine with chlorine or nitric acid (Rochleder, Annalen, 71, 1); (2) by reducing dimethylalloxan with sulphuretted hydrogen (Fischer, Ber. 1881, 14, 1912) or with stannous chloride (Andreasch, Monatsh. 1895, 16, 19); (3) from dimethyldialuric acid and dimethylalloxan (Maly and Andreasch, Monatsh. 1882, 3, 105); (4) by the electrolysis of caffeine in sulphuric acid solution (Pommerehne, Arch. Pharm. 235, 365). *See* Biltz (Ber. 1912, 45, 3673) for the preparation of *dimethyl* and *tetramethylalloxantin* from theobromine and caffeine respectively. *Tetraethylalloxantin* $C_{16}H_{22}O_8N_4$, obtained by reducing diethylalloxan, melts and decomposes at 162° (Sembritzki, Ber. 1897, 30, 1821).

M. A. W.

ALLOXAZINE *v.* ALLOXAN.

ALLOYS *v.* METALLOGRAPHY.

ALLYL. A univalent radicle C_3H_5—, or $CH_2:CH\cdot CH_2$—, isomeric with *propenyl* $CH_3\cdot CH:CH<$.

Allyl acetate $CH_3\cdot CO_2C_3H_5$ boils at 103°–104°/733·9 mm. (Brühl), and has sp.gr. 0·9376 at 0° (Schiff). It is only slightly soluble in water, and has a rather sharp smell. It is prepared by the action of allyl iodide on silver acetate (Zinin, Annalen, 96, 361; Cahours and Hofmann, Annalen, 102, 295; Brühl, Annalen, 200, 179; Schiff, Annalen, 220, 109).

Allyl acetic acid $C_3H_5\cdot CH_2\cdot CO_2H$ boils at

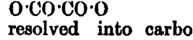
187°–189°, and has sp.gr. 0·98416 at 15° (Perkin). It is slightly soluble in water and its smell resembles that of valerianic acid. It is unaffected by reduction with sodium amalgam, but readily unites with two atoms of bromine. It is prepared by hydrolysing allyl acetoacetic acid ethyl ester with dry sodium ethoxide, or by heating allyl malonic acid (Zeidler, Annalen, 187, 39; Conrad and Bischoff, Annalen, 204, 170; Henry, Chem. Zentr. 1898, ii. 663).

The *chloride* $C_3H_5·CH_2·COCl$ is a thick, pungent-smelling syrup, boiling at 128°/765 mm., and of sp.gr. 1·0739 at 16° (Henry, *l.c.*).

Allylacetone $CH_3·CO·CH_2·C_3H_5$ boils at 128°–130°, and has sp.gr. 0·834 at 27°. It is an unpleasant-smelling liquid. It forms an amorphous compound with sodium bisulphite, and is reduced by sodium amalgam to hexenyl alcohol. It is prepared by hydrolysing allyl acetoacetic acid ethyl ester (70 grams) with crystallized baryta (215 grams) and water (1650 c.c.) (Zeidler, Annalen, 187, 35; Merling, Annalen, 264, 323). Treated with hydroxylamine it yields *allylacetoxime* $CH_3·C(:NOH)·CH_2·C_3H_5$, which is a liquid boiling at 188° (corr.), soluble in alcohol, benzene, ether, acids and alkalis.

Allyl alcohol $C_3H_5·OH$, *i.e.* $CH_2:CH·CH_2·OH$ occurs in raw wood spirit, but only to the extent of about 0·2 p.c. (Aronheim, Ber. 1874, 1381; Grodzki and Kramer, *ibid.* 1492). It is a pungent liquid with a burning taste, and mixes readily with alcohol, water, or ether. It boils at 96·6° (corr.), and has sp.gr. 0·87063 at 0° and 0·8573 at 15°/15° (Thorpe, Chem. Soc. Trans. 1880, 208), D_0 0·86929, and b.p. 96·95° (Wallace and Atkins, Chem. Soc. Trans. 1912, 1183).

It is prepared by slowly distilling glycerol (400 parts) with crystallised oxalic acid (100 parts) and a little ammonium chloride (1 part) to convert any potassium oxalate into chloride. The receiver is changed at 190° and distillation continued up to 260°. It is usually stated that the allyl alcohol is produced by the decomposition of monoformin, but according to Chattaway, the chief source is the normal oxalic ester dioxalin



$$\begin{array}{l} CH_2\text{——}CH·CH_2OH, \\ \,| \qquad\quad\;\; | \\ O·CO·CO·O \end{array}$$

which on heating is resolved into carbon dioxide and allyl alcohol (Chattaway, Chem. Soc. Trans. 1914, 105, 151; *ibid.* 1915, 107, 407). The distillate, containing aqueous allyl alcohol, allyl formate, acrolein, and glycerol, is rectified and dried, first with potassium carbonate, then over solid potash and distilled. When the last traces of water are removed by quicklime it boils at 96·6°. The yield is one-sixth of the weight of oxalic acid taken (Tollens and Henninger, Bull. Soc. chim. [2] 9, 394; Brühl, Annalen, 200, 174; Linnemann, Ber. 1874, 854). Further purification may be effected by prolonged heating with sodium bisulphite and, after removal of the bisulphite, redistilling several times from quicklime (Thorpe).

According to Koehler (Bull. Soc. chim. 1913, [iv.] 13, 1103) the yield of allyl alcohol may be increased from 20 to 32 p.c. by replacing the oxalic acid by formic acid. 100 grams of glycerol are heated with 80 grams of formic acid for an hour on a water-bath and the product fractionally distilled and collected in three fractions: (1) up to 200°; (2) 200°–260°; (3) residue. The saponification index of fraction (2) is determined, and it is then poured on to twice the calculated amount of solid potassium hydroxide. The whole is boiled for an hour, allowed to cool, and the top layer decanted and dried over anhydrous potassium carbonate. The intermediate product is monoformin.

According also to Hoff (K. Danske Videnskab. Selskab. Forhand. 1915, 199) the most satisfactory method of preparing allyl alcohol consists in the direct reduction of glycerol with formic acid. 825 grams of 97 p.c. glycerol and 84·2 grams of 95 p.c. formic acid (mol. props. 5 : 1) are heated together in a retort; the receiver is changed at 200°, and the distillate collected between 200° and 250°. After cooling a further quantity of 165 grams of glycerol and 84·2 grams of formic acid is added, and the distillation carried out as before. This process is repeated ten times. From the distillate between 200° and 250°, which weighs about 1470 grams, allyl alcohol is obtained after treatment with potassium carbonate, the yield being about 54 p.c., calculated either with respect to the glycerol or the formic acid (Chem. Soc. Abstr. 1916, i. 6).

Allyl alcohol is oxidised by chromic acid solution to acrolein and formic acid; and by dilute nitric acid to formic and oxalic acids; whilst potassium permanganate produces acrolein, glycerol, and formic acid. It combines directly with chlorine, bromine, iodine chloride, and cyanogen, producing additive products. It is partially reduced by boiling for some hours with zinc and dilute sulphuric acid to *n*-propyl alcohol. Potassium displaces the hydroxylic hydrogen atom and forms gelatinous potassium allylate.

Denigès (Bull. Soc. chim. 1909, 5, 878) describes the following colour reactions for the detection of allyl alcohol, depending on the formation of (1) glyceraldehyde and (2) dihydroxyacetone and the condensation of these products with various reagents. Bromine water (0·6 c.c. in 100 c.c. water) is added to 0·1 c.c. of allyl alcohol, till a slight permanent colouration is produced, and the liquid is then boiled, cooled, and divided into portions of 0·4 c.c. To each of these 0·1 c.c. of a 5 p.c. solution of codeine, resorcinol, thymol, or β-naphthol is added, followed by 2 c.c. of sulphuric acid (sp.gr. 1·84) and the mixture warmed during 3 or 4 minutes at 100°. Codeine and thymol give reddish-violet colourations, resorcinol wine-red, and β-naphthol yellow with greenish fluorescence. The second series of colour reactions is obtained by adding to the brominated liquid above described 5 c.c. of bromine water (0·6 c.c. in 100 c.c. water), heating during 20 minutes at 100°, then boiling to remove excess of bromine and cooling. This liquid contains dihydroxyacetone, and in the presence of concentrated sulphuric acid gives a deep-blue colour with codeine, orange-red with resorcinol, blood-red with thymol, or green with green fluorescence with β-naphthol (Denigès, Compt. rend. 148, 172, and 282).

Bromine is quantitatively absorbed by allyl alcohol, whether the former is in excess or not, and the reaction is suitable for the exact quantitative estimation of the alcohol, which may be effected either by direct titration with bromine water until a permanent yellow colouration is obtained, or by treating the acidified aqueous solution of the alcohol with an excess of bromide-bromate solution, followed by addition of potassium iodide and titration of the liberated iodine with sodium thiosulphate (Stritar, Monatsh. 1918, 39, 617).

Allylamines.

Monoallylamine $C_3H_5{\cdot}NH_2$ is a liquid boiling at 53·3° and of sp.gr. 0·7799 at 4° and 0·7688 at 15° (Perkin, Chem. Soc. Trans. 1889, 697); b.p. 58° and sp.gr. 0·864 at 15° (Rinne, Annalen, 168, 262); b.p. 56°–56·5°/756·2 mm. (Schiff, Ber. 1886, 565). It is prepared from allyl *iso*cyanate and potash, or from allyl iodide and ammonia, or by reduction of allyl mustard oil with zinc and hydrochloric acid (Oeser, Annalen, 134, 8). It possesses a penetrating smell, which excites tears and produces sneezing. It is miscible with water in all proportions, and is a strong base, forming a crystalline platinichloride $(C_3H_5{\cdot}NH_2)_2PtCl_4$, and sulphate $(C_3H_5{\cdot}NH_2)_2H_2SO_4$. The hydrochloride melts at 105°–110° (Delépine, Bull. Soc. chim. [3] 17, 294) and the picrate at 140°–141° after sintering (Gabriel and Eschenbach, Ber. 1897, 1125).

Diallylamine $(C_3H_5)_2NH$ boils at 111° and is prepared from allylamine and allyl bromide (Ladenburg, Ber. 1881, 1879; Liebermann and Hagen, Ber. 1883, 1641).

Triallylamine $(C_3H_5)_3N$ is a very unpleasant-smelling liquid, boiling at 150°–151° (Pinner, Ber. 1879, 2054); 155°–156°, sp.gr. 0·8094 at 14·3° (Zander, Annalen, 214, 151). It is prepared by distilling tetrallylammonium bromide with large excess of recently fused potash (Grosheintz, Bull. Soc. chim. [2] 31, 391) or from allyl chloride and alcoholic potassium cyanide in the cold (Pinner, *l.c.*); or from allyl chloride and ammonia (Malbot, Bull. Soc. chim. [2] 50, 90). It is displaced from its aqueous solution by potash, and forms a crystalline platinichloride and hydrochloride.

Tetrallylammonium bromide $(C_3H_5)_4NBr$ is a crystalline solid, soluble in alcohol and water, but only slightly so in ether. It is prepared by leading a stream of ammonia into an alcoholic solution of allyl bromide. The product is purified by recrystallisation from alcohol containing a little ether (Grosheintz, Bull. Soc. chim. [2] 31, 390). Treated with moist silver oxide it yields tetrallylammonium hydroxide.

Tetrallylammonium iodide $(C_3H_5)_4NI$ is the main product of the reaction of allyl iodide on ammonia at the ordinary temperature (Cahours and Hofmann, Annalen, 102, 305; Malbot, Ann. Chim. Phys. [6] 13, 488). It is a crystalline solid, insoluble in strong potash solution.

Allylaniline $C_6H_5{\cdot}NHC_3H_5$ is a yellow oil produced by the action of allyl iodide on aniline. It boils at 208°–209° and has sp.gr. 0·982 at 25° (Schiff, Annalen Suppl. 3, 364).

Diallylaniline $C_6H_5{\cdot}N(C_3H_5)_2$ is prepared by adding allyl bromide (1 mol.) to aniline (1 mol.) in a flask fitted with reflux condenser, separating the allyl aniline by the addition of potash, and converting it into diallyl aniline by repeating the process with more allyl bromide (1 mol.). It boils at 243·5°–245°, and has sp.gr. 0·9538 at 19·8° (Zander, Annalen, 214, 149).

Allyl benzene $C_6H_5{\cdot}CH_2{\cdot}CH{:}CH_2$ is obtained zinc-dust to 100° (Chojnacki, J. 1873, 559; Fittig, Annalen, 172, 312). It boils at 155°. The isomeric *propenyl benzene* (and phenyl propylene—$C_6H_5{\cdot}CH:CH{\cdot}CH_3$) is sometimes incorrectly referred to as allyl benzene.

Allyl bromide, *monobrompropylene* $CH_2{:}CH{\cdot}CH_2Br$, boils at 70°–71°, and has sp.gr. 1·4336 at 17° (Zander, Annalen, 214, 144); b.p. 70·5° (corr.) (Thorpe). It is formed by the action of phosphorus tribromide on allyl alcohol, and is prepared by dropping allyl alcohol into a hot solution of potassium bromide in sulphuric acid (1 vol. acid to 1 vol. H_2O) according to Grosheintz (Bull. Soc. chim. [2] 30, 78); or by saturating allyl alcohol with hydrogen bromide at 0° and subsequently heating to boiling for several hours (Jacobi and Merling, Annalen, 278, 11).

Allyl bromide absorbs hydrogen bromide in bright light forming trimethylene bromide; in the dark propylene bromide is also produced (Holleman and Matthes, Proc. K. Akad. Wet. Amster. 1918, 21, 90).

Allyl chloride $CH_2{:}CH{\cdot}CH_2Cl$ boils at 46°, and has sp.gr. 0·9547 at 0° (Tollens, Annalen, 156, 154); 0·9371 at 19·3° (Zander, Annalen, 214, 142); b.p. 45·29° (corr.) (Thorpe). It is prepared by the action of mercuric chloride on allyl iodide, or from allyl oxalate calcium chloride and alcohol at 100° (Oppenheim, Annalen, 140, 205); or, best, by heating allyl alcohol and concentrated hydrochloric acid to 100° for some hours (Eltekow). It combines with hydrogen chloride to form *propylene chloride* $C_3H_6Cl_2$, and with fuming hydrobromic acid yielding 1-chloro-3-bromopropane $CH_2Cl{\cdot}CH_2{\cdot}CH_2Br$

Allyl cyanamide, *sinamine*, $C_3H_5{\cdot}NH{\cdot}CN$, is produced by warming allyl thiocarbamide with lead hydroxide on the water-bath (Will, Annalen, 52, 15). On standing for some months crystals separate from the resulting product. It is prepared by shaking an aqueous solution of allyl thiocarbamide with mercuric oxide until the solution no longer blackens ammoniacal silver nitrate (Andreasch, Monatsh. 2, 780). It is alkaline in reaction, precipitating metallic oxides and replacing ammonia in its salts. The crystals contain $\frac{1}{2}H_2O$ and melt at 100°, giving up their water. It forms a difficultly crystallisable salt with oxalic acid, but not with other acids, and double compounds with mercuric and platinic chlorides.

Allyl cyanide, *crotononitrile*, $C_3H_5{\cdot}CN$, boils at 119° (corr.), and has sp.gr. 0·8491 at 0° and 0·8351 at 15°. It is obtained by the action of allyl iodide on potassium cyanide, and, together with other products, by allowing allyl mustard oil to remain in contact with water for some weeks, and also by the action of acetic anhydride on crotonaldoxime. It has been prepared by Henry (Chem. Zentr. 1898, ii, 662) by the action of phosphorus pentoxide on *a*- or *β*-hydroxy-butyronitrile. It is a liquid with an unpleasant, onion-like smell. On warming to 50°–60° with fuming hydrochloric acid for two hours, chlorobutyric acid is produced. Chromic acid oxidises it to acetic acid, nitric acid to oxalic acid.

Allylenes. Two allylenes are possible and known: symmetrical allylene $CH_2{:}C{:}CH_2$, and unsymmetrical allylene $CH_3{\cdot}C{:}CH$.

Symmetrical allylene, *propadiene*, $CH_2:C:CH_2$, flame. It is prepared by dropping α-bromoallyl bromide (10 grams) into a mixture of 20 grams zinc-dust and 25 grams alcohol (70 p.c.) (Gustavson and Demjanow, J. pr. Chem. [2] 38, 202). It does not precipitate ammoniacal solutions of silver nitrate or cuprous chloride. It is readily absorbed by strong sulphuric acid, and acetone is produced on dilution. When dissolved in absolute ether and heated with sodium to 100°, it changes into the isomeric methyl acetylene It readily forms a tetrabromide $C_3H_4Br_4$ by addition of bromine.

Unsymmetrical allylene, *methyl acetylene* $CH_3C{:}CH$, results from propylene bromide, monobromopropylene, or monochloropropylene by withdrawal of HCl or HBr by means of alcoholic potash, and from symmetrical allylene (*v. supra*). It is an unpleasant-smelling gas, which is liquefied under a pressure of 3–4 atmospheres. It burns with a bright sooty flame. It dissolves readily in ether (30 vols. in 1 of ether at 16°). Potassium permanganate in the cold oxidises it to formic, oxalic, and malonic acids. Explosive compounds are produced by leading it into ammoniacal solutions of silver nitrate or cuprous chloride. Concentrated sulphuric acid readily absorbs it, forming on dilution and distillation acetone mesitylene and allylene sulphonic acid $C_3H_3SO_3H$ (Schrobe, Ber. 1875, 18 and 367). The *barium salt* of the latter is crystalline, easily soluble, and not decomposed on boiling with water. *Cf.* ACETYLENE: homologues of.

Allyl ether $C_3H_5\cdot O\cdot C_3H_5$ boils at 94·3° and has sp.gr. 0·8046 at 18°. It is prepared from allyl iodide and sodium allyl alcoholate, or from allyl iodide and mercuric oxide (Cahours and Hofmann, Annalen, 102, 290; Berthelot and Luca, Ann. Chim. Phys. [3] 48, 291).

Allyl ethyl ether $C_3H_5\cdot O\cdot C_2H_5$ boils at 66°–67°/742·9 mm. (Brühl, Annalen, 200, 178). Prepared from allyl iodide and sodium ethoxide.

Allyl iodide C_3H_5I boils at 102·79° (corr.) (Thorpe and Rodger), and has sp.gr. 1·8696 0°/0°. Berthelot and Luca (Ann. Chim. Phys. [3] 43, 257) obtained it by the action of PI_2 on glycerol. It may be prepared by leaving together for 24 hours red phosphorus (20 grams), allyl alcohol (160 grams), and iodine (254 grams) (Tollens and Henninger, Annalen, 156, 156); or by the following process: 100 grams of iodine and 1500 grams of carefully dehydrated glycerol are brought together in a large vessel, the air displaced by a current of carbon dioxide, and 300 grams of ordinary phosphorus gradually added. The allyl iodide is distilled off in a stream of carbon dioxide, and then contains as impurity some *iso*propyl iodide. According to Rasik Lal Datta (J. Amer. Chem. Soc. 1914, 36, 1005) the use of carbon dioxide is unnecessary. To purify it, it is dissolved in alcohol and shaken with mercury, when the compound HgC_3H_5I is precipitated. This is recrystallised from water and decomposed, regenerating allyl iodide, by distillation with water and the theoretical quantity of iodine (Linnemann, Annalen Suppl. 3, 263). It combines with bromine to form tribromhydrin, and with hydriodic acid to give diiodopropylene. By long heating with about 20 parts of water it is converted into allyl alcohol and hydriodic acid.

Allyl mercaptan C_3H_5SH boils at 90°. With mercuric chloride it yields C_3H_5SHgCl, which crystallises from alcohol in plates (Hofmann and Cahours, Annalen, 102, 292; Gerlich, Annalen, 178, 88).

Allylmethylal *iso***thiocyanate** is the name given to the compound $C_3H_5O\cdot S\cdot CH_2\cdot CN$, prepared by passing a current of formaldehyde gas through glycerol (1 kilo) and allyl *iso*thiocyanate (5 grams) heated to 190° until the weight of the whole is 1400 grams. When cool the product is filtered and the resulting methylal *iso*thiocyanate used as an antiseptic (Piot, Fr. Pat. 330988, 1903).

Allyl mustard oil *v.* MUSTARD OIL and ESSENTIAL OILS.

Allyl nitrite $C_3H_5NO_2$ is obtained by adding glycerol trinitrite to ice-cold allyl alcohol and cautiously distilling off the allyl ester (Bertoni, Gazz. chim. ital. 15, 364). It boils at 43·5°–44·5°, and has sp.gr. 0·9546 at 0°. It is readily decomposed by shaking with water, and yields ethyl nitrite on treatment with ethyl alcohol.

Allyl-phenyl-thiourea $SC\!<\!\begin{smallmatrix}NH\cdot C_3H_5\\ NH\cdot C_6H_5\end{smallmatrix}$ may be prepared from aniline and mustard oil (Zinin, Annalen, 84, 348); or from allylamine and phenyl mustard oil (Weith, Ber. 8, 1529). It forms monoclinic crystals, melting at 98°, and is readily soluble in ether, but not in water.

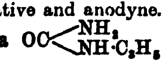
Allyl pyrrol $C_4H_4NC_3H_5$ is readily obtained by the action of allyl bromide on potassium pyrrol in ether (Ciamician and Dennstedt, Ber. 1882, 2581). It is a light-yellow oil, turning brown on exposure to air. It boils at 105°/48 mm. It is insoluble in water, but dissolves in HCl, producing a red colour.

Allyl sulphate $C_3H_5\cdot HSO_4$ is prepared by adding allyl alcohol (1 vol.) to sulphuric acid diluted with its own volume of water (1 vol.), and leaving at ordinary temperatures for five days. Subsequently the mixture is heated to 70° for 12 hours, diluted with water (10 vols.), and saturated with barium carbonate (Szymanski, Annalen, 230, 44; *v.* also Cahours and Hofmann, Annalen, 102, 293). It forms characteristic salts, a number of which are described by Szymanski (*l.c.*).

Allyl sulphide, *oil of garlic,* (Ger. *Knoblauchöl*) $(C_3H_5)_2S$, occurs in garlic (*Allium sativum*) and other plants. It is prepared from mustard oil and potassium sulphide at 100° (Wertheim, Annalen, 55, 297); or from allyl iodide and potassium sulphide (Hofmann and Cahours, Annalen, 102, 291). It is a liquid boiling at 138·6°, and has sp.gr. 0·88765 at 26·8°/4°. It has a very strong odour of garlic and is only slightly soluble in water.

Allyl thiocarbamide, *allyl thiourea, thiosinamine, 'Rhodallin'* $SC\!<\!\begin{smallmatrix}NH_2\\ NH\cdot C_3H_5\end{smallmatrix}$, is produced by the prolonged action of aqueous ammonia on mustard oil (Dumas and Pelouze, Annalen, 10, 326). It forms clear six-sided tables, which melt at 78·4°, after sintering at 71°. It is insoluble in benzene, sparingly soluble in water, and readily so in alcohol and ether. It combines directly with halogens, cyanogen, ethyl iodide, acids, &c. Deprived of its sulphur by mercuric oxide, or lead oxide, it yields *sinamine* (allyl cyanamide) $C_3H_5\cdot NH\cdot CN$. It has been used in surgery for the removal of scar tissue, being injected as a 10 or 15 p.c. solution in dilute glycerol.

Allyl tribromide, '*Tribromhydrin*' $C_3H_5Br_3$, was obtained by Wurtz by treating allyl iodide with bromine, and by Berthelot and Luca by the action of phosphorus tri- and pentabromides on glycerol. It is a slightly yellow liquid of sp.gr. 2·430 at 15·5°, and boils at 217°. It is a strong sedative and anodyne.

Allyl urea 
$OC\begin{cases}NH_2\\NH{\cdot}C_3H_5\end{cases}$ crystallizes in needles, melting at 85° (Cahours and Hofmann, Annalen, 102, 299; Andreasch, Monatsh. 5, 36).

J. A. P.

ALMASCA. A soft grey resin soluble in chloroform, ether, and absolute alcohol. Probably derived from the burseraceous *Protium heptaphyllum* (March.) [*Icica heptaphylla* (Aubl.)] (Symes, Pharm. J. [3] 13, 213).

ALMATEIN. Trade name for a condensation product of hæmatoxylin and formaldehyde. Used as an antiseptic.

ALMIRAO. Indian name for *Launœa pinnatifida* (Cass.) *Microrhynchus sarmentosus* (DC) which belongs to the family Compositæ and is used at Goa as a substitute for taraxacum (Dymock, Pharm. J. [3] 6, 730).

ALMOND. The kernel of the fruit of *Prunus amygdalus* or *Amygdalus communis*.

Two principal varieties exist—the sweet and the bitter almond. Both contain amygdalin, but the latter is much richer in this substance (2 to 3 p.c.), and contains an enzyme, *emulsin*, which, in the presence of water, decomposes the amygdalin. yielding glucose, benzaldehyde, and hydrocyanic acid

$$C_{20}H_{27}NO_{11}+2H_2O$$
$$=C_6H_5CHO+HCN+2C_6H_{12}O_6$$

In addition, almonds contain about 50 p.c. of their weight of a fixed oil (mainly oleïn, and liable to become rancid) and smaller quantities of proteïns, sugar, starch, gum, fibre, and ash.

Analyses of almonds made at various stages of growth and ripening, show the percentage of amyloses, glucose, and saccharose to steadily diminish, whilst the proportion of oil increases (Du Sablon, Compt. rend. 1896, 123, 1084).

According to Vallée (Compt. rend. 1903, 136, [2] 114), reducing sugars in the immature almond decrease as the fatty oil increases: sucrose increases until oil-formation begins, then decreases during oil-production, and towards the end again increases. Ripe almonds contain about 3 p.c. of sucrose. According to Osborne and Campbell (J. Amer. Chem. Soc. 1896, 18, 609), the proteïn in almonds is *amandin* and not conglutin or vitellin.

H. I.

ALMOND OIL is obtained from the seeds of *Prunus amygdalus* (Stokes) [*Amygdalus communis* (Linn.)]. The almond tree appears to have been indigenous to Turkestan and Middle Asia, and has been transplanted from there to Greece, Italy, Spain, France, and to Northern Africa. The mean percentage composition of the almond is given by König as follows:—

Oil	41·00	p. c.
Water	27·72	„
Proteins	16·50	„
Extracted matter, free from nitrogen	10·20	„
Crude fibre	2·81	„
Ash	1·77	„

The commercial oil is chiefly expressed from bitter almonds, the seeds of *Prunus amygdalus*, var. *amara*. Bitter almonds contain, besides the oil, amygdalin and emulsin, which give rise to the formation of benzaldehyde, dextrose, and hydrocyanic acid. Hence the press-cakes from almonds find a profitable outlet in the manufacture of genuine 'ethereal bitter almond oil,' which is prepared by triturating the meal with water.

Sweet almonds (from *Prunus amygdalus*, var. *dulcis*) are but rarely used alone for the preparation of almond oil. Mogador bitter almonds, which are chiefly used in this country for the manufacture of almond oil, are always more or less mixed with sweet almonds. Sweet almonds yield from 44 to 55 p.c. of oil, bitter almonds yield less and may contain as low a proportion of oil as 20 p.c. On an average, however, bitter almonds yield from 38 to 45 p.c. of oil.

The oil is pale yellow; it has a very pleasant, mild taste, and is almost free from odour. The specific gravity of the oil varies from 0·915 to 0·9195 at 15°. The oil becomes turbid at −10°, and solidifies at −20°, has the saponification value of the majority of oils which are free from volatile acids, and an iodine value of 93–100. Farnsteiner (Zeitsch. Nahr. Genussm. 1899, 2, 1) separated linolic tetrabromide in a proportion corresponding with 5·97 p.c. of linolic acid, and it is probable that other specimens may contain up to about 10 p.c. of that acid. The other fatty acids consist mainly of oleic acid, with, at most, traces of saturated fatty acids.

Almond oil is chiefly used in pharmaceutical practice. Owing to its high price it is largely adulterated with other oils of the *Prunus* family, chiefly with apricot kernel oil, from *Prunus armeniaca* (Linn.), and with peach kernel oil, from *Prunus persica* (Sieb. et Zucc.). These two oils are very similar to almond oil, but have a less pleasant taste. They are used to such an extent as adulterants that frequently they completely take the place of almond oil; indeed 'foreign' almond oil, or 'oil of sweet almonds, French' (*Oleum amygdalarum gallicum*), is nothing else than a mixture of apricot kernel oil and peach kernel oil. Genuine almond oil is sold in commerce under the name 'almond oil, English.'

The close relationship in which apricot and peach kernel oils stand to almond oil, renders their detection in almond oil a difficult problem. They differ from almond oil in sometimes having a higher iodine value (96–108), and a higher critical temperature of solution (*e.g.* almond oil, 32°–33·5°; apricot kernel oil, 46°–47°; and peach-kernel oil, 41°). Of various colour reactions that of Bieber (Zeitsch. anal. Chem. 1878, 17, 264) is the best known. It depends on the different colourations given by the three oils when shaken with a mixture of strong sulphuric and nitric acids and water. The chromogenic substance in apricot kernel oil is not volatile with steam, and the test is capable of detecting 5 p.c. of that oil in almond oil (Ross and Race, Analyst, 1911, 36, 263).

ALMONDS, BITTER, *Essential oil of* (*v.* BENZALDEHYDE; also OILS, ESSENTIAL).

ALOE. A genus of succulent plants, having

Liliaceæ. (Plants figured, and structure of leaves described, Pennetier, 560, 579.) Of the 85 species 60 are natives of Cape Colony, and the other species are mainly sub-tropical African, though a few occur in the tropics; a number of species have been, however, introduced into the West and East Indies. (For a list of the species and their distribution, *v.* Pharm. J. [3] 11, 746.)

The fibre is used for rope, &c.; experiments made in Paris have shown it to be five times as strong as hemp. The fibre has also been used for paper-making (Nat. 20, 484).

ALOE-EMODIN *v.* RHUBARB.

ALOE RESINS *v.* ALOES OR BITTER ALOES.

ALOES or BITTER ALOES. (*Aloès*, Fr.; *Aloe*, Ger.; *Aloe*, B.P.; U.S.P.). The inspissated juice or extract of the aloe. Slow concentration induces crystallisation and gives an opaque product 'aloe hepatica.' More complete and rapid evaporation yields glassy 'aloe lucida,' which shows no crystals under the microscope. The principal varieties found in the market are:—

1. *Curaçao* (*Barbados*) *Aloes* (from *A. chinensis*, Baker, *A. vera*, L.), formerly produced in Barbados, but now almost exclusively in Curaçao and other Dutch West Indian islands. It is usually opaque ('livery') and from orange to nearly black in colour.

2. *Cape Aloes* (from *A. ferox*, Miller, and other South African species) is vitreous, breaking readily into transparent glassy, reddish, or pale-brown fragments. It is the chief variety used in Germany and adjoining countries; in Britain mostly for veterinary purposes.

3. *Socotrine Aloes* (from *A. Perryi*, Baker). It is generally imported in a moist pasty condition, and is of a dark reddish-brown colour. A variety of Socotrine Aloes from Zanzibar often closely resembles that from Curaçao. Of these, Curaçao Aloes is the only one containing appreciable quantities of *iso*barbaloin, and hence gives Klunge's reaction characteristic for this substance (*see* below). With concentrated nitric acid Curaçao aloes become at once deep red; Socotrine becomes reddish- or yellowish-brown; Cape aloes gradually green. The aqueous solution (1 p.c.) of all varieties shows a green fluorescence on adding 5 p.c. borax solution. Natal aloes is no longer an article of commerce; Uganda aloes (imported from Mossel Bay) is a variety of Cape aloes produced by careful evaporation.

Aloïns. By extracting aloes with water the purgative principles, aloïns, can be obtained. Shenstone (Pharm. J. [3] 13, 461; Chem. Soc. Trans. 44, 480) divides them into two classes: 1. *Nataloïns*, which only yield picric and oxalic acids with nitric acid, and which are not reddened by it, even on heating (Flückiger, Arch. Pharm. [2] 149, 11; Tilden, Chem. Soc. Trans. 25, 153). 2. *Barbaloins*, which yield aloetic acid $C_{14}H_4(NO_2)_4O_2$, chrysammic acid $C_{14}H_2(NO_2)_4(OH)_2O_2$, picric and oxalic acids, and are reddened by nitric acid. *a-Barbaloïns*, from Barbados aloes reddened in the cold by strong nitric acid (Tilden, Pharm. J. [3] 2, 845; Chem. Soc. Trans. 25, 488). *β-Barbaloïns*, from Socotrine, Zanzibar, and Jafferabad aloes, coloured only on heating with ordinary, and in the cold with fuming, nitric acid (Flückiger, *l.c.*; Tilden, Chem. Soc. Trans. 28, 1270; Pharm. J. [3] 4, 208).

Aloïn, official in the B.P. and U.S.P., and obtained chiefly from Curaçao aloes, is a yellow crystalline powder consisting of a mixture of *barbaloïn* and *isobarbaloïn*, which substances, according to Léger (Compt. rend. 1911, 153, 114), are isomeric, having an arabinose group in positions 1 and 8 respectively. Léger (J. Pharm. Chim. 1907, [vi.] 25, 476, 513) further, considers that all the above-mentioned varieties of aloes yield barbaloïn with the exception of the Natal variety, which gives a separate substance, nataloïn. The amount of aloïn in Curaçao aloes has been variously estimated as from 10 to 30 p.c. In addition, there is present an amorphous aloïn (*β-barbaloïn*), which is apparently stereoisomeric with crystalline barbaloïn, and is formed from the latter by heating for three hours to 160°–165°, and partly by acetylation (Léger, Compt. rend. 1914, 158, 1903). Cape aloes contain 5–6 p.c. of crystalline barbaloïn and about three times the amount of β-barbaloïn (Léger, Compt. rend. 1907, 145, 1179).

Tschirch and Pedersen (Arch. Pharm. 236, 200) found in Barbados aloes 12·25 p.c. barbaloïn, 12·65 p.c. resin, 1·75 p.c. ash, 10·5 p.c. amorphous constituents soluble in water, and 0·15 p.c. *aloe emodin* (which is a fission product of barbaloïn, *see* below; its constitution and properties are given under RHUBARB). The resin is the cinnamate of aloeresinotannol $C_{22}H_{24}O_4(OH)_2$(?). According to Tutin and Naunton (Pharm. J. 1914, [iv.] 37, 836) the proportion of aloe emodin is much larger.

Barbaloin may be readily prepared by extracting aloes with two parts of water at 90°–95°; the crystals, which separate on standing for some days, are recrystallised from water, and finally from alcohol. It forms small yellow prismatic needles containing water of crystallisation, and when anhydrous, melting at about 147°.

Barbaloïn has formed the subject of numerous investigations. For a long time its formula was considered to be $C_{16}H_{18}O_7$ (Tilden, Trans. 1872, 25, 204; 1875, 28, 1270; Schmidt, Ber. 1875, 8, 1275), or $C_{16}H_{16}O_7$ (Groenewold, Arch. Pharm. 1890, 228, 115; Léger, Compt. rend. 1897, 125, 185). Aschan (Arch. Pharm. 1903, 241, 341) and Jowett and Potter (Chem. Soc. Trans. 1905, 87, 878) confirmed one or other of these formulæ by molecular weight determinations, as well as by analysis. Against this mass of evidence we must, however, place Léger's observation (Compt. rend. 1902, 134, 1111, 1584), that by the action of sodium peroxide on barbaloïn, there are formed formic acid, *aloe-emodin* $C_{15}H_{10}O_5$ (*see* RHUBARB), and an aldopentose $C_5H_{10}O_5$. He accordingly changed the formula to $C_{21}H_{20}O_9$. Later he showed (Compt. rend. 1910, 150, 983, 1695; 1912, 155, 172) that alcoholic hydrogen chloride also produces aloe-emodin and the sugar, which was confirmed by Oesterle and Riat (Schweiz. Woch. Chem. Pharm. 1909, 717). Finally, Léger identified the sugar with certainty as *d-arabinose*; he considers that in barbaloïn it is attached to the aloe-emodin in position 1, and in *iso*barbaloin in position 8 of the anthraquinone; the sugar is, moreover, attached by one of its hydroxyl groups and not by the aldehyde group as in other glucosides.

Seel and Kelber (Ber. 1916, 49, 2364) have confirmed Léger's formula by molecular weight determinations (*cf.* also Seel, Kelber, and Scharf, Ber. 1917, 50, 759).

The only way of reconciling Léger's results with the C_{16} formula would be to regard barbaloïn as a reduced anthraquinone derivative, which breaks down by two simultaneous but independent reactions to aloe emodin and *d*-arabinose, but it is preferable to attribute the earlier analytical results to the difficulty of purifying the substance.

Barbaloïn, after several crystallisations from alcohol, does not show a sharp melting-point (145°–150°), $[a]_D$ −10·4° in ethylacetate (Léger), −8·3° in 90 p.c. alcohol (Jowett and Potter).

Aloe-emodin $C_{15}H_{10}O_5$, m.p. 224°, is an alcohol, a hydroxymethyl dihydroxyanthraquinone (for constitution and relationships, *see* under RHUBARB). On oxidation with chromic acid barbaloïn gives a mixture of aloe-emodin and the corresponding acid, rhein (Oesterle and Babel, Schweiz. Woch. Chem. Pharm. 1904, 42, 329), which mixture was named by Tilden (Chem. Soc. Trans. 1879, 32, 264, 903) aloexanthin.

Isobarbaloin occurs, according to Léger, in Barbados aloes to the extent of 0·5 p.c.; it gives the same hydrolytic products as barbaloin, and the two are therefore regarded by Léger as stereoisomeric (Compt. rend. 1910, 150, 1695) It gives Klunge's reaction (*see* above), and is not present in Socotrine and Cape aloes.

Nitric acid (D 1·2 at 100°) oxidises both barbaloïn and *iso*barbaloin to tetranitroaloe-emodin $C_{15}H_6O_5(NO_2)_4$ (Léger, Compt. rend. 1910, 151, 1128; 1911, 153, 114), which by boiling nitric acid (D 1·32) is converted into chrysammic acid $C_{14}H_2O_2(OH)_2(NO_2)_2$. In the mother-liquor of the tetranitroaloe-emodin Léger found 2:4:6-trinitro-3 hydroxybenzoic acid, which by loss of carbon dioxide yields picric acid. In addition to picric and chrysammic acids the older observers obtained aloetic acid by the action of nitric acid on aloin; Oesterle and Riat (Schweiz. Woch. Chem. Pharm. 1906, 44, 509) consider aloetic acid to be trinitroaloe-emodin.

Natal aloes contains about 14 p.c. of *nataloin*, m.p. 203°, crystallised from boiling ethyl or methyl alcohol. Among the various formulæ assigned to this substance probably the best established is that of Léger (J. Pharm. Chim. 1903, [vii.] 17, 13), $C_{23}H_{26}O_{10}$, who regards it as the methyl ether of *homonataloin* $C_{22}H_{23}O_9 \cdot OH$, also present in the drug. The latter, and probably also the former, of these aloins, like barbaloin, yield *d*-arabinose on hydrolysis (Léger, Compt. rend. 1912, 155, 172), which is apparently less stably attached than in barbaloin to a *tri*hydroxymethylanthraquinone, *nataloemodin*, orange-red needles, m.p. 220°, and its methyl ether.

Nataloemodin methylether, pale orange-yellow needles, m.p. 238°, is formed by the oxidation of nataloïn with sodium peroxide (Léger, J. Pharm. Chim. 1903, [vii.] 17, 13, 52). Nataloin differs from barbaloïn in its resistance to alkalis, and in not yielding chrysammic acid or aloexanthin on oxidation with nitric acid, but only picric and oxalic acids (Shenstone, Chem. Soc. Trans. 44. 480); further, in not giving Klunge's and Borntraeger's reactions (*see* below). Both nataloïn and its lower homologue give a green colouration with concentrated sulphuric acid and manganese dioxide or potassium dichromate, and a violet colouration in sodium hydroxide solution with ammonium persulphate (Léger). For a general review of the more recent work on the chemistry of the aloins, *see* Léger, Ann. Chim. 1916, [ix.] 6, 318–381.

The resin from Natal aloes yields on hydrolysis *p*-coumaric acid and nataloresinotannol $C_{22}H_{18}O_4(OH)_2$ (?).

Sicaloin is a crystalline substance from aloes of *Aloe vulgaris*, native in Sicily. Condò-Vissicchio has given it the formula $C_{15}H_{20}O_7$, and finds it to contain one methoxy group; it does not fluoresce with borax, and does not give Borntraeger's reaction (below).

The aloins from Curaçao, Cape Socotra, Uganda, and Jafferabad aloes are probably identical with barbaloin. *Zanaloin* from Zanzibar aloes appears to be different (Léger, J. Pharm. 25, [vi.] 513; Tschirch and Hoffbauer, Arch. Pharm. 243, 399). The latter chemists show that Barbados aloes contain but little *iso*aloin, Jafferabad none, whilst that from Curaçao contains a considerable proportion.

Uses.—Chiefly in medicine and as a hop-substitute. In doses of 0·1–0·3 gram aloin causes purgation in 8–20 hours, given by the mouth or hypodermically. In the latter case, it is excreted in the large intestine, where it probably is first oxidised to an active substance. The oxidation is hastened by iron salts, whence the use of *Pilula Aloes et Ferri*. Aloes is the basis of most 'patent' pills.

Various proposals have been made for converting aloin into (insoluble and) tasteless compounds, *e.g.* by condensation with formaldehyde in dilute sulphuric acid solution ('formaloïn' of E. Merck), with carbonyl chloride or ethyl chlorocarbonate in pyridine solution (Ger. Pat. 229191), or with a mixture of formic and acetic acids by means of zinc chloride (Ger. Pat. 233326).

Properties and Reactions.—Pure aloes is soluble in ether and almost completely soluble in water, the solution being coloured dark-brown by alkalis, black by ferric chloride, and grey by lead acetate (Flückiger). By adding a solution of copper sulphate or chloride to a solution of aloes, an intense yellow-coloured solution is obtained, which, warmed with potassium bromide or chloride, turns to a deep-red and reddish-violet tint (Klunge, Ber. 16, 691; Arch Pharm. 1883, 363). This reaction is due to *iso*barbaloin, for barbaloin, recrystallised several times from methyl alcohol, does not give the test (Léger, Compt. rend. 131, 55). Borntraeger (Zeitsch. anal. Chem. 19, 165; Ber. 13, 1040) extracts with twice the volume of benzene, and adds to the clear extract a drop of ammonia, when, on warming and shaking, the solution becomes violet-red; to test for aloes in elixirs, liqueurs, &c., the alcohol is first evaporated. This is a general reaction for hydroxymethyl anthraquinones. Lenz (Zeitsch. anal. Chem. 21, 220) extracts with amyl alcohol, evaporates the extract, treats with nitric acid, and then with potassium cyanide and hydroxide, when a blood-red colouration is obtained. Cripps and Dymond (Pharm. J. [3] 15, 633) test for aloin by dissolving 1 grain in 16 drops of strong sulphuric acid, then adding 4 drops of nitric acid (1·42) and 1 ounce of water, when a deep orange or crimson colour is produced, deepened by ammonia; substances containing chrysophanic acid behave in a similar manner, but their aqueous solution turns pink upon the addition of ammonia. Aschan (Arch. Pharm. 241, 340) gives in tabular form a comparison of the reactions of the chief varieties of aloes. The behaviour towards nitric acid and fluorescence with borax are mentioned above.

Curaçao aloes should be almost entirely soluble in 60 p.c. alcohol, and contain not more than 3 p.c. of ash, 12 p.c. of moisture, and 30 p.c. of substances insoluble in cold water. Cape aloes should dissolve almost completely in 12 parts of boiling water, and completely in 5 parts of warm 90 p.c. alcohol. The moisture should not exceed 5 p.c., the ash 1·5 p.c. At least 60 p.c. is soluble in cold water. According to the U.S.P. the ash of aloes does not exceed 4 p.c.

A process for the estimation of aloin in aloes has been described by Schaefer (J. Pharm. [vi.] 5, 296), and for the non-resinous constituents by Tschirch and Hoffbauer (Arch. Pharm. 1905, 243, 399). The latter process has been modified and used by van Itallie (Pharm. Weekblad, 1905, 42, 553) for the evaluation of aloes, but in the nature of things these processes are not very accurate. G. B.

ALOES, ESSENTIAL OIL OF. A pale-yellow mobile liquid to which the odour of aloes is due. Sp.gr. 0·863, boils at 266°–271°. It exists in small quantities in aloes, and when pure has the taste and odour of peppermint (Pharm. J. [3] 10, 613).

ALOES WOOD. A name applied to the wood of *Aquillaria Agallocha* (Roxb.), a leguminous tree of Cochin China, and to that of *A. malaccensis* (Lam.) of tropical Asia. Both are highly fragrant and aromatic; used in fumigations and pastilles, and occasionally by cabinet-makers and inlayers.

The same name is applied to the resin. Of all perfumes this is said to be the most esteemed by Orientals.

ALOIN *v.* Glucosides.

ALOO BOKHARA, ALPOGADA, PAZHAM. The Bokhara plum (*Prunus insititia* (Linn.) [*P. bokhariensis*], largely imported into Bombay. Used as a laxative. The root is astringent; the gum is used as a substitute for gum arabic under the name of Persian gum (Dymock, Pharm. J. [3] 9, 145).

ALOUCHI RESIN *v. Aluchi resin*, art. Resin.

ALPHOGEN (Alphozone). Trade names for succinyl peroxide.

ALPHOL *v.* Synthetic drugs.

ALPINIA OFFICINARUM *v.* Galanga root.

ALPINIA OIL. An essential oil obtained from the leaves of *Alpinia malaccensis*; sp.gr. 1·02 at 26°, rot. power +6·5°. Consists mainly of methyl cinnamate, together with *d*-pinene (Van Romburgh, Proc. K. Acad. Wetensch. Amsterdam, 1900, 3, 451).

ALPININ *v.* Galanga root.

ALPOGADA *v.* Aloo bokhara.

ALQUIFON. Black lead ore or Potters' ore. A native lead sulphide, used by potters to glaze coarse ware.

ALSOL *v.* Synthetic drugs.

ALSTONIA BARK. The dried bark of *Alstonia scholaris* (R. Br) and *A. constricta* (F. Muell.), an apocynaceous tree growing in Australia. It has a bitter taste, slightly camphorous odour, contains a neutral bitter principle (similar to *cailcedrin* and *tulucumin*), a volatile oil smelling like camphor, an iron-greening tannin, resin, fat, wax, a protein-like substance, oxalic and citric acids (Palm, J. 1863, 615).

Muller and Rummel (Chem. Soc. Trans. 35, 31) obtained a yellow substance to which they gave the name *alstonine*. Oberlin and Schlagdenhauffen (Pharm. J. [3] 10, 1059; Chem. Soc. Abstr. 38, 127) showed that this body consisted of two compounds, *alstonine* and *alstonicine*, the former being soluble in acids with fluorescence, the latter without.

Hesse subsequently (Ber. 14, 264; Annalen, 205, 360) isolated:

Alstonine (chlorogenine) $C_{20}H_{21}N_2O_4$, a brown amorphous mass, a strong base, soluble in chloroform, alcohol, and sparingly soluble in ether, and melting when anhydrous at 195° (uncorr.).

Porphyrine $C_{21}H_{25}N_3O_2$, a white powder melting at 97° (uncorr.), soluble in alcohol, chloroform, ether, and acids, with blue fluorescence.

Porphyrosine, soluble in acetic acid, forming a pink solution.

Alstonidine, colourless needles, melting at 181° (uncorr.), soluble in chloroform, ether, alcohol, and acetone.

Hesse, however, could not find a trace of quinine (Ber. 11, 1546, 1753).

ALSTONIA SPECTABILIS. *Poelé bark.* Contains *alstonamine* (Hesse, Ber. 11, 1548), and the alkaloids of dita bark. It contains six times as much echitammonium hydroxide as dita bark (Hesse, Annalen, 203, 144).

Its physiological action is like that of curare.

ALSTONINE. One of a series of ill-defined alkaloids occurring in *Alstonia* spp. (Hesse, Annalen, 1880, 203, 147; 205, 360), including *alstonamine*, *alstonidine*, *ditaine*, *ditamine*, &c.

ALSTONITE. A rare mineral consisting of barium and calcium carbonate $(Ba,Ca)CO_3$, crystallising in the orthorhombic system. The small crystals have the form of acute six-sided pyramids, and consist of complex twin intergrowths. Found, associated with witherite, in 1834 in a lead- and zinc-mine near Alston in Cumberland, and at Fallowfield in Northumberland; and in 1909 in a coal-mine near Durham. This species is often, but incorrectly, called bromlite (*cf.* Barytocalcite). L. J. S.

ALTHEIN. *See* Anthocyanins. The term *Althein* is used also as syn. for Asparagin.

ALTI. Indian name for a root used at Goa as a substitute for Althæa (Dymock, Pharm. J. [3] 8, 101).

ALUDEL. The aludels of the earlier chemists were pear-shaped pots generally made of earthenware, but sometimes of glass, open at both ends. Each aludel had a short neck at the top and bottom, so that a series of them could be fitted together by means of the necks. The earthenware pear-shaped vessels in which the mercurial vapours are condensed at Almaden in Spain are also known as aludels.

ALUM *v.* ALUMINIUM.

ALUMINATES *v.* ALUMINIUM.

ALUMINIUM. Sym. Al. At. wt. 27·1.

Occurrence.—Aluminium is the most widely distributed element in nature with the exception of oxygen and silicon. It is not found in the metallic state.

As oxide, Al_2O_3, aluminium is found in *corundum*, or, coloured by metallic oxides, in *sapphire*, *ruby*, *emery*, &c. The hydrated oxide Al_2O_3,H_2O occurs as *diaspore*, and, together with ferric oxide, silica, &c., as the important mineral *bauxite*.

Aluminium occurs in combination with oxygen and metals as *aluminates*, in *spinel* $Al_2O_3{\cdot}MgO$, *chrysoberyl* $Al_2O_3{\cdot}BeO$, *gahnite* $Al_2O_3{\cdot}ZnO$. As hydrated sulphate it is found in *aluminite* or *websterite* $Al_2O_3SO_3,9H_2O$, and as *alunogen* $Al_2O_3(SO_3)_3,18H_2O$; as the double sulphate of aluminium, potassium, and sodium in *alumstone* or *alunite*; and, as an efflorescence on aluminous minerals in the form of the alums of potassium, sodium, ammonium, &c.

Aluminium occurs principally, however, as silicate in the various *clays*; as silicate containing silicon fluoride in the *topaz*; and, as double silicate, with iron, magnesia, lime, &c., in *garnets*; with potassium, sodium, magnesium, and calcium in immense quantities in the varieties of *felspar*.

As double fluoride of aluminium and sodium it is found in *cryolite* $Al_2F_6{\cdot}6NaF$; as hydrated phosphate in the *turquoise* and in *wavellite*, and as borate in a crystalline mineral occurring in Siberia.

Although present in such quantities in the soil, aluminium is not usually considered a constituent of the ash of plants except of cryptogams; Yoshida, however (Chem. Soc. Trans. 1887, 748), has found it in a number of phanerogams in Japan.

History.—The name of this metal is derived from *alumen*, a term applied by the Romans to all bodies of an astringent taste. Pott, in 1746, stated that the basis of alum is an argillaceous earth; and in 1754 Marggraf pointed out the distinction between alumina and lime, and its presence in combination with silica in clay.

Davy, in 1807, having isolated the alkali metals by electricity, endeavoured, unsuccessfully, to reduce alumina in the same manner.

Oersted, in 1824, prepared aluminium chloride by passing chlorine over a mixture of alumina and carbon heated to redness. He appears to have reduced the chloride to the metallic condition by heating with potassium amalgam: (Berzelius, Jahresb. 1827, [6] 118). The amalgam produced oxidised rapidly in the air, and left, on volatilising the potassium, a tin-white metal.

Wöhler, in 1827 (Annalen, 1828, 37, 66), having failed to procure the metal by Oersted's method, obtained it by the decomposition of the *anhydrous* chloride with potassium, as a grey powder, which became brilliant under the burnisher.

Bunsen and Deville, in 1854, independently, obtained the metal by electrolysis of the fused chloride. Deville, in the same year, much simplified the manufacture by substituting sodium for the more expensive potassium. In 1854 he was installed in the manufactory of Javel by the Emperor Napoleon III., and supplied with the necessary apparatus for experiments on the large scale. Afterwards his process was removed to Nanterre and finally to Salindres. A description of his method is given in Ann. Chem. Phys. [3] 43, 5–36, and specimens of the metal produced were shown at the Paris Exhibition of 1855.

Shortly after the publication of these results, Messrs. Dick and Smith, under the direction of Dr. Percy, prepared aluminium by the action of sodium on the then newly discovered mineral *cryolite*, some of the product being shown by Faraday at the Royal Institution in March, 1855 (Phil. Mag. 10, 365).

About six months subsequently, Rose, independently, prepared it in the same manner, and published his results in an extended article in P. 96, 152 (Phil. Mag. 10, 233).

Deville at once turned his attention to this process (Ann. Chim. Phys. [3] 46, 451); but on account of the impurity of the metal produced, he preferred the double chloride of aluminium and sodium, using cryolite as a flux only.

The first manufactory in England was started at Battersea, London, in 1859, by F. W. Gerhard. Some of his metal was shown at the Society of Arts Exhibition in 1860. Messrs. Bell, of Newcastle, also prepared aluminium and aluminium bronze in 1863, using Netto's process. A mixture of 200 lbs. of cryolite and an equal weight of common salt was brought to fusion, and 40 lbs. of sodium gradually added. The charge thus contained only 5 p.c. of aluminium, but less than half of this was obtained in the yield.

The manufacture ceased in 1874. In Grabau's process (J. Soc. Chem. Ind. 1891, 433) aluminium fluoride was subjected to the action of metallic sodium. Other modifications were proposed from time to time, but the production of aluminium made no notable advance. Weldon, in 1883, summed up the position of the industry in the statement that 'the only method known for the manufacture of aluminium is Deville's. M. Pechiney has improved and cheapened the modes of working, and the appliances for carrying that method into effect, but this is all the progress which has been made in the manufacture of aluminium during the last five and twenty years.'

When the great stability of the available compounds containing aluminium is considered, it is not to be wondered at that the many attempts that have been made to prepare the metal by the action of the usual reducing agents, such as carbon, hydrogen, or hydrocarbons, have met with so little success. The heat of formation of these compounds is an index to their stability, and may be taken as a measure of the energy requisite for the isolation of the aluminium. The operation is not likely to succeed unless the elements which become separated from the aluminium enter into new combinations of still greater stability. The nature of the changes that might be expected to take place may be expressed in the following equations:—

$$\begin{array}{rrcl} & 2Al_2O_3 + 3C & = & 4Al + 3CO_2 \\ \text{or} & Al_2O_3 + 3C & = & 2Al + 3CO \\ & Al_2O_3 + 6H & = & 2Al + 3H_2O \\ & Al_2O_3 + 6Na & = & 2Al + 3Na_2O \\ & Al_2Cl_6 + 6H & = & 2Al + 6HCl \\ & Al_2Cl_6 + 6Na & = & 2Al + 6NaCl \\ & Al_2F_6 + 6Na & = & 2Al + 6NaF. \end{array}$$

In order that there may be a likelihood of these reactions occurring, the heat arising from the formation of the compounds on the right hand should exceed the heat concerned in the decomposition of the aluminium compounds on the left. The following table will show how far this is the case:—

	Calories		For amount equivalent to 2Al
Al_2O_3	391,600	$\frac{3}{2}CO_2$	145,500
		3CO	86,400
		$3H_2O$	174,900
		$3Na_2O$	302,700
Al_2Cl_6	323,600	6HCl	132,000
		6NaCl	587,400
Al_2F_6	558,000	6NaF	604,200

It will be seen that only the last two reactions will be at all likely to take place, and these heat values indicate that sodium is a much more favourable reagent than carbon or hydrogen, and that the highest excess of heat evolved over that absorbed occurs in the case of the aluminium chloride in presence of sodium.

The following analyses, taken from Hoffmann's Ber. Entwick. Chem. Ind. (1) 603, show the composition of commercial aluminium as produced under Deville's process:—

	1	2	3	4	5	6	7	8	9	10
Locality . .	Paris	Paris	Berlin	Paris	Paris	Paris	Bonn	Nanterre (Morin)		
Analyst . .	Salvétat	Salvétat	Mallet	—	Dumas	Dumas	Kraut	Kraut	Kraut	Sauerwein
Aluminium .	88·35	92·97	96·25	92·60	92·5	96·16	94·7	—	—	97·2
Silicon . .	2·87	2·15	0·45	0·45	0·7	0·47	3·7	0·04	0·12	0·25
Iron . .	2·40	4·88	3·29	7·55	6·8	3·37	1·6	1·62	2·26	2·40
Copper . .	6·38	—	—	—	—	—	—	—	—	—
Lead . .	trace	—	—	—	—	—	—	—	—	trace
Sodium . .	—	trace	trace	—	—	—	—	—	—	—

Moissan has shown (Compt. rend. 121, 851) that it contained also from 0·1 to 0·5 p.c. of sodium; 0·3 to 0·4 p.c. of carbon and other impurities. These impurities would have a very considerable effect on the properties of the metal, and statements based on observations with such metal, or even metal now being made, must be accepted with due regard to these impurities.

The production even in 1885 was small and did not exceed 2½ tons at Salindres and 2½ cwt. in the United States.

According to Mallet, pure aluminium may be prepared by the method adopted by him in his determination of the atomic weight of that element (Phil. Trans. 171, 1018). Ordinary commercial aluminium is converted into bromide by the direct action of bromine. On account of the violence of the action, the metal should be immersed only for a short time, at intervals, until dissolved, or should be added in very small pieces. The bromide so produced is freed from bromine by distillation and fractionally distilled, that portion boiling uniformly at 263·3° being reserved. This portion is colourless, entirely soluble in water, and consists of the pure bromide.

It is heated with sodium (which has been carefully freed from oil and well scraped) in a crucible made of a mixture of pure alumina and sodium aluminate. The amount of sodium used should not be sufficient to reduce the whole of the bromide, or the aluminium is liable to contain sodium. The globules of metal are fused together before the blowpipe on a bed of alumina, immersed for a short time in hydrochloric acid, washed and dried. Pure aluminium might also be produced by the electrolysis of the pure bromide or chloride.

The purification from metallic impurities on the large scale involves many difficulties. The only method of obtaining satisfactory metal is to ensure as high a state of purity as possible in the first instance by making use of selected materials and avoiding contamination in the process of manufacture.

By the establishment of Deville's process the price of aluminium had been brought down from 18*l.* per lb. to 1*l.*, at which it stood till 1887.

The double chloride of sodium and aluminium used contained only 14 p.c. of aluminium, and the working of large charges with a small yield together with the high cost of sodium and fuel stood in the way of any prospect of reduction in the price of the metal.

The introduction of Castner's process, by which sodium could be produced much more cheaply, led to the establishment of the Aluminium Company's works at Oldbury, and effected some reduction in the price of aluminium. Meanwhile Messrs. Cowles (Patents Aug. 18, 1885, and Jan. 26, 1886) brought electrical heating into operation, and, though their process was not adapted to the production of aluminium, it was capable of furnishing alloys of aluminium with copper and other metals. These could be made at one-tenth the price which had ruled for aluminium, and the valuable properties of aluminium bronze, Hercules metal, and other alloys were soon recognised. Moreover, the discovery of the effect of the addition of minute amounts of aluminium to iron and steel gave a further stimulus to the production of aluminium. C. W. Siemens had already described an electric furnace (1881) capable of giving very high temperatures, and the type of furnace patented by Messrs Cowles Bros. was based on similar lines.

The furnace is a rectangular box, one foot wide, five feet long, and fifteen inches deep, all inside measures. Two carbon electrodes pass through pipes in the ends; they are three inches in diameter and thirty inches long; this size could not be exceeded, as larger carbons disintegrated under the intense heat. For a non-conducting furnace lining, fine particles of charcoal are washed in lime-water, exposed to the air and dried. They thus become coated with lime and are of good insulating power. At the high temperature produced, ordinary charcoal becomes converted into graphite and forms a good conductor. The two electrodes being within a few inches of one another, the charge of twenty-five parts of corundum, twelve parts of carbon, and fifty parts of granulated copper is placed around and between them, covered with small lumps of charcoal, and the whole covered with an iron top lined with fire-brick. The current from a powerful dynamo is then passed, and the electrodes moved if necessary to produce the requisite resistance. In about ten minutes, the copper having melted between the electrodes, the distance between them is increased while the current is raised to 300 amperes of fifty volts E.M.F. and the yield 1 lb. per E.P.H. hour. As the resistance is increased, the temperature rises, the alumina is reduced to the metallic condition and alloys with the copper, while its oxygen forms carbon monoxide and burns at the openings in the cover with a white flame. After about five hours the operation is completed The alloy produced is brittle, consisting of copper and 15 p.c. or upwards of aluminium. When boron or silicon oxides have been added, the bronzes produced contain these elements. It is melted, cast into ingots, the percentage of aluminium determined, and sufficient copper added to produce 'aluminium bronze,' or the required alloy.

When other metals, such as iron, nickel, silver, &c., are substituted for copper, corresponding alloys are produced.

The slag produced is hard and compact, but soon falls to a fine alkaline powder; it contains alumina, calcium aluminate, with traces of copper, silicon, &c.

Pure aluminium cannot be produced satisfactorily by this method, as it remains, to a great extent, mingled with the carbon.

See further, W. P. Thompson (J. Soc. Chem. Ind. 1886, 206); Mabery (Amer. J. Sci. 308, and Amer. Chem. J. 1887, 11).

The Electrical Process.—A new principle was, however, introduced into metallurgy, and the application of electricity for purposes of heating and reduction of metals has made rapid progress in recent years. Its full development had not, however, been reached in the process just described. It had been shown that, though the fusion of a substance like alumina could not be economically effected owing to its high resistance, the addition of copper and other metals enabled the furnace charge to conduct the current. If a suitable solvent could be found for alumina then the electrolytic action of the current could be brought into play. When this was accomplished the chemical method of decomposition would give place to the electrolytic method, and the isolation of aluminium become a question of a sufficient current at the necessary voltage. This voltage can readily be calculated from the heat of formation of the compound in question by dividing the number of calories per equivalent by 23,250. We thus obtain for alumina 2·81 volts, for aluminium chloride 2·32 volts, for aluminium fluoride 4·00 volts, for aluminium sulphide 0·9 volt.

A suitable solvent is found in native cryolite $3NaF{\cdot}AlF_3$, which may be brought to fusion below 1000°, and will dissolve 15 to 20 p.c. of its weight of alumina, and in this condition, also owing to high temperature, the voltage is lower—in the case of alumina about 2·3 volts.

In the year 1886 the Héroult process was patented and soon came into use at Neuhausen, and at the Société Electrométallurgique at Froges, near Grenoble. In this process the anodes consisted of carbon and the cathode was the carbon lining of the furnace, the distance between the anode and cathode being capable of adjustment by raising or lowering the anode. The cryolite was first melted in the bath by utilising the heat generated by the resistance to the electric current, and then alumina was added, and the additions continued from time to time as the bath became exhausted. The metallic aluminium settled at the bottom of the bath in the neighbourhood of the cathode, and was tapped every 24 hours.

The purity of the metal at first was 97–99 p.c. There were at disposal 360 kilowatts at Froges, and just over 1000 kilowatts at Neuhausen (J. Soc. Chem. Ind. 1892, 910); the yield usually obtained was about 1½ lbs. of aluminium per kilowatt-day, an efficiency of less than 25 p.c. To-day 35 p.c. efficiency is reached.

The Hall process, brought out in the United States about the same time, only differed from Héroult's in matters of detail, the anodes being rods of carbon 3 inches in diameter, or of larger dimensions in sections banded together, the electrolyte being alumina dissolved in mixed fluorides of calcium and aluminium or $AlF_3{\cdot}NaF$.

Minet (Compt. rend. 112, 231) used a bath composed of 62·5 p.c. of common salt and 37·5 p.c. of cryolite, but his metal seems to have contained 2 to 3 p.c. of impurity, which was chiefly silicon, owing largely to the impurity of the alumina used by him. Aluminium so prepared was liable to contain sodium, owing to the fact that the voltage necessary for the decomposition of aluminium fluoride differed so little from that required to decompose sodium fluoride—viz. 4·7 as against 4.

There was added to the bath as the operation proceeded, a mixture of hydrated alumina, cryolite, and alumina dissolved in cryolite.

Kleiner invented a furnace for the decomposition of cryolite, and carried on the production of aluminium at Tyldesley in Lancashire; a plant was also operated on the lines of the Héroult system at Patricroft near Manchester.

In this case the dynamos were run by steam power, and it soon became manifest that this could not compete with advantageous supplies of water power which began to be called into requisition wherever such power was available.

Mention should also be made of the method of Bucherer, D. R. P. 63995 (1892), who prepared aluminium by electrolysing the double sulphide of aluminium and an alkali or alkaline earth, the chief obstacle to success being the expense and difficulty attending the production of the sulphide.

It soon became evident that the Hall and

Héroult process must hold the field, and that coal could not compete with cheap water power in this industry, and rapid expansions of the industry were made. The price had by 1891 been brought down to one-fifth of that which had ruled under Deville's process, and the production had increased to over 300 tons per annum. The accompanying statement is the cost of production at this period, as given by A. E. Hunt (Eng. and Mining Journ. 1891, 280). For 1 lb. of aluminium there was requisite

2 lbs. alumina	costing 6 cents
1 lb. carbon electrode	„ 2 „
Chemicals, pots, &c.	„ 1 „
22 E.H.P one hour	„ 5 „
Labour, interest, repairs	„ 5 „

making 19 cents in all.

The following firms were at this period manufacturing either aluminium or its alloys:—

In England—
- Cowles Syndicate (Cowles process).
- Reduction Syndicate (Hall process).

In the United States—
- Pittsburg Reduction Company.
- Cowles Electric Smelting Company.
- United States Aluminium Metal Co.

On the Continent—
- Société Electrométallurgique at Froges.
- Aluminium Industrie Actien-Gesellschaft at Neuhausen.

Further progress was mainly in the direction of increasing the yield and bringing down the cost of production whilst perfecting the various details of the process so that a purer product could be made.

We shall now describe the further development of the industry and the manufacture as it stands to-day after over 20 years of experience; and in doing so it will be well to consider in greater detail (*a*) the production of alumina, (*b*) the making of the carbon electrodes, (*c*) the nature and arrangement of plant, including the reduction furnaces.

Development of the Aluminium Industry—The first factory established on electrical lines was that started in 1888, at New Kensington, by the Pittsburg Company, which is now known as the Aluminium Company of America, and conducts operations at the Niagara Falls, the Shawinigan Falls, and at Massena.

Amongst the pioneers of the industry were also (1) Aluminium Industrie Aktien-Gesellschaft, who control works at Neuhausen, Rheinfelden, and Lend Gastein; (2) the British Aluminium Company, with reduction works operating in 1896 at Foyers and now at Kinlochleven (Argyllshire), and branch works at Larne, Burntisland, Warrington and Milton (Staffordshire),—this company is also associated with reduction works at Stangfiord and Vigelands Brug (Norway), and projected works at Orsières (Switzerland); (3) Société Electrométallurgique Française at Froges, La Praz, and St. Michael, and the Cie. des Produits Chimiques d'Alais et de la Carmargue.

There were formerly works on a smaller scale under the Aluminium Corporation at Wallsend, now in operation at Dolgarrog (N. Wales), and developments in Italy at Bussi. The cost of production of the metal to-day is said to be 61*l.* per ton as a minimum, though at most works it would reach 80*l.* (Mining World, June 26, 1909). For the past five years costs have been much higher.

The market price of aluminium ingots in 1902-4 was 120*l.* per ton, but it rose to 200*l.* in 1906, and has since then fallen to 65*l.* (1909), though it is now again advancing. Since 1902 no trustworthy record has been made of the world's output of aluminium. It remained, however, fairly stationary in the neighbourhood of 8000 tons from 1900 to 1905 inclusive, and since then has grown steadily, and may be estimated for 1909 at 30,000 tons. In the United States Geological Survey publications (Metallic Products) for 1908 there may be found the estimated consumption of metal in the United States, from which it appears that in 1907 this amounted to nearly 7700 tons, and in 1908 to nearly 5000 tons.

The following is a statement of the production of aluminium in metric tons from 1889 to 1913, (*a*) in the United States and Canada, (*b*) total output:—

	a	*b*
1889	22	93
1890	28	193
1891	68	302
1892	118	505
1893	154	870
1894	250	1491
1895	417	1835
1896	591	2250
1897	1814	5220
1898	2359	6860
1899	2948	8950
1910	17400	43800
1911	20500	45000
1912	29200	63000
1913	32300	68000

During the period of the war, 1914 to 1918, the data available are incomplete and hardly to be depended upon. Considerably increased outputs are, however, recorded. In 1917 there appear to have been about 79,500 tons manufactured in the United States and Canada with 168,000 tons as total output. France in that year produced about 20,500 tons; Germany, who in 1913 produced only 800 tons, put down during the war large instalments of plant sufficing for 40,000 tons; the British production was 13,000 tons and that of the other European countries 15,000 tons. Switzerland is stated to have exported nearly 10,000 tons per annum into Germany. Norway made large extensions in reduction works which did not become effective owing to lack of raw materials. In other directions her efforts in electrochemical developments have been such as to command 125,000 kilowatts in 1917 as compared with 9000 kilowatts in 1904.

The Production of Alumina.—The raw material from which the alumina is usually made is bauxite, deposits of which occur at Beaux and in the Var (S. France), at Feistritz (Austria), Wochein (Styria), Irish Hill (Ireland), Georgia, Arkansas, Alabama, Tennessee (United States), British Guiana, and in New South Wales. The physical condition of the bauxite varies considerably, so that some kinds are more readily acted upon for the production of alumina than others. In the aluminium industry a low content of iron and silica is desired,

especially the latter; it is therefore usually found advantageous to employ the red bauxites, the white bauxites being used preferably in the manufacture of sulphate of alumina. The following table gives the composition of typical samples :—

Locality .	Beaux		Var		Wochein		Feistritz			Irish	Georgia
			Red	White	Dark coloured	Light coloured	Reddish brown	Yellow	White	Raw	
Al_2O_3 .	60	75	50–62	65–74	63·16	72·87	44·4	54·1	64·6	35·0	60·5
Fe_2O_3 .	25	12	24–28	0·3–3	23·55	13·49	30·3	10·4	2·0	38·0	1·9
SiO_2 .	3	1	1–7	12–18	4·15	4·25	15·0	12·0	7·5	3·5	3·3
H_2O .	12	12	12–13	14	8·34	8·50	9·7	21·9	24·7	21·5	32·1
TiO_2 .	—	—	0·1–4	—	trace	trace	—	—	—	2·0	2·2

The following analyses by Leop. Mayer and O. Wagner (Dingl. poly. J. 248, 213) show that the appearance of bauxite cannot be relied on as a criterion of its value. The origin of the samples is not given :—

	Appearance	Hygroscopic moisture	Combined water	Al_2O_3	Fe_2O_3	SiO_2	MnO_2	CaO	MgO	P_2O_5
1	Pure white .	2·33	13·86	29 80	3·67	44·76	—	2·75	0·84	1·47
2	Yellow . .	1·03	27·85	43·22	14·39	10·43	—	1·61	—	1·13
3	„ . .	1·30	27·70	50·38	11·68	8·34	trace	trace	trace	0·61
4	Red . .	1·34	23·12	33·86	25·69	12·41	2·42	trace	—	0·53
5	„ . .	1·31	23·81	46·18	22·05	4·82	—	0·89	—	0·66
6	„ . .	0·95	20·83	62·10	6·11	5·06	2·01	3·20	trace	trace
7	„ . .	1·17	4·75	21·80	3·75	60·10	—	6·06	2·49	trace

The amount of bauxite mined in 1907 was 260,000 tons, three-fifths of which was produced in France. In 1913 the production was 533,000 tons distributed as follows: United States 210,000, France 309,000, Great Britain 6000, other countries 8000. During the period 1914–1918 no reliable returns are available, but it is certain that the output was much larger. That for the United States alone was 569,400 tons in 1917, and British production 15,000 tons. New deposits were opened up in Dalmatia and Hungary, the latter country contributing 59,000 tons in 1915. Increased production of aluminium and aluminium salts account for 457,000 tons. The more recent applications of bauxite to the production of alundum, abrasives and refractory materials for bricks and furnace linings took up 112,400 tons.

For the manufacture of the purest form of alumina the bauxite is first roughly powdered and calcined to get rid of water and any organic matters. It is then more finely ground and introduced gradually with agitation into kiers containing caustic soda solution of 1·45 sp.gr. The kiers are now closed and the charge heated for some hours under high-pressure steam—about 70–80 lbs. The contents of the kiers are then transferred to the filter presses, and the filtrate further cleared through wood pulp in lead-lined vats. The liquor contains sodium aluminate $NaAlO_2$, which may be decomposed by passing carbon dioxide into it, but it is now more usual to adopt the Bayer method of precipitating the alumina. This method depends on the fact that the addition of alumina effects the decomposition of the aluminate and throws down some 70 p.c. of the alumina. The dissolved liquor now contains alumina and soda in the proportion $Al_2O_3 : Na_2O :: 1 : 6$. The precipitated hydrate of alumina is allowed to settle, and the liquor with its undecomposed portion is run off into weak-liquor tanks. The hydrate is filter-pressed, sufficent being left in the vat to serve as precipitant for the next charge. The weak liquor may, after concentration, be used over again for reacting upon a further amount of bauxite.

The press cake containing the impurities removed in the treatment of bauxite constitutes usually over 30 p.c. of the bauxite, whether the wet process of extraction or the dry fusion process with sodium carbonate be used. In the latter case, the residue has been successfully applied in the removal of sulphuretted hydrogen from coal—or from exit gases of other products. The residue from the wet process is, however, inactive in this respect, but may be transformed into a condition in which it is very effective.

The hydrate of alumina so obtained ought to contain less than 0·5 p.c. of mineral impurity, iron and silicon being the more objectionable impurities. To bring it into a suitable physical condition for use in the reduction furnaces it must be calcined at 1100°–1200°, so that it shows no tendency to give up moisture when used in the furnace or to absorb moisture when exposed to air.

The alumina of to-day is superior to that of twenty years ago, and the cost of production less than one-half. It constitutes, however, about one-fifth of the whole cost of manufacture of aluminium, and many processes have been brought forward with a view to improve or cheapen the product. Of these may be mentioned the patents of Peniakoff (Eng. Pat. Nov. 19, 1895, Mar. 18 and May 13, 1896, &c.). Endeavours have been made to obtain alumina of sufficient purity from bauxite, clay, felspar, or kaolin by electrically heating them with iron (or its oxide), carbon and cryolite, thus separating ferrosilicon from alumina; Moldenhauer (J. Soc. Chem. Ind. 1909, 148), Sinding-Larsen (*ibid.* 1908, 409), Tone (Electrochem. and Metallurg. Ind. 1909, 35), Hall (J. Soc. Chem. Ind. 1902, 49). Recently Serpek has proposed to prepare alumina by forming the carbide and acting upon this with producer gas consisting of 77 p.c. nitrogen, 23 p.c. carbon monoxide, and a little carbon dioxide. He claims that a tolerably pure nitride of aluminium is formed, and this decomposed by steam yields alumina and ammonia (Journal du Four Electrique, 315, 1; J. Soc. Chem. Ind. 1911, 26; Fr. Pat. 405712 and 418059). Many other patents have been taken out with the object of producing alumina or nitride with the use of clay or other crude materials in place of the purified alumina, or as means of procuring alumina. Amongst these may be mentioned Cowles' process (Journal du Four Electrique, 1913, 176), Child's process (Met. and Chem. Eng. 1913, 231), Peacock's proposal to use felspar (*l.c.*), the Badische patent (Chem. Trade Journ. April, 1911), as well as methods of extraction from alunite with the recovery of alkaline salts (Waggaman and Cullen, J. Soc. Chem. Ind. 1916, 1217), and Hershmann (U.S. Pat. 1915 and 1916). Serpek's process has also undergone considerable developments in operations on the large scale at St. Jean de Maurienne. *See* also J. Soc. Chem. Ind. 1913, 509; Met. and Chem. Eng. 1913, 137.

The Making of Carbon Electrodes.—Bituminous coal, anthracite, retort carbon, natural or artificial graphites, soot and oil-coke are all materials which have from time to time been used in the production of carbon electrodes. In deciding which of these materials should be used, account must be taken of: (*a*) Supply and cost of raw material; (*b*) ash content; (*c*) amount of volatile matter and sulphur; (*d*) conductivity for electricity and heat. It must also be understood that electrodes used for the production of aluminium differ in character from those used for lighting or for the production of calcium carbide and many other purposes where graphitisation of the carbon is an advantage and the presence of mineral matter is quite permissible and even necessary. The graphitisation of amorphous carbon, which must contain mineral impurities, is indeed effected by exposing it to a high temperature under electrical heating.

It is said that at the temperature employed the iron volatilises. Be this as it may, the ash of such carbon contains a considerable amount of oxide of iron. Aluminium, boron, silicon, and other elements which form carbides can be used as graphitising agents, as also to some extent the oxides of these elements.

Graphite or graphitised electrodes have at 1000° C. about 5 times the electrical conductivity of coke blocks and 8 to 10 times the thermal conductivity, but it is now recognised that these properties, advantageous in some respects, are not, however, favourable to the efficient working of reduction furnaces.

It may be taken that, so far as it is capable of reduction in the aluminium furnace, the mineral ash contained in the carbon alloys itself with the aluminium, as also the foreign matter present in the alumina. The amount of alumina used should be about double that of the aluminium resulting therefrom, and the electrode consumption about one-half of the aluminium, so that an estimate may be made of the impurity as silicon contained in the metal. Assuming the silica in the alumina and in the electrode together as 0·4 p.c., in each case, the amount of silicon in the metal will be very nearly 0·2 p.c.

Similar considerations apply to the iron content of the metal, though this may, by reason of operations, much exceed the amount of iron contributed by the alumina and electrodes.

The electrical resistance is in microhms per cubic inch of

	0°	1000°
Amorphous carbon (pressed)	1·63	1·45
Graphite carbon . . .	0·42	0·25
Electrodes for aluminium .	3·00	2·60

The resistance per cubic centimetre would be 2·54 times these values. (For further detail, The Electric Furnace, Stansfield, or the pamphlet issued by the Acheson Graphite Co., may be consulted; also Met. and Chem. Eng. 1915, 23.) In addition to low resistance to the electrical current, it is desirable that electrodes should be of low conductivity for heat, that they should be sufficiently hard and resistant to superficial oxidation, of low porosity and of as even character as possible throughout their whole mass.

To produce electrodes having these qualities the material (oil coke, pitch coke, and anthracite, used separately or mixed) must be carefully selected, ground, calcined, and subjected to high pressure with the admixture of tar or other material to act as binder. The blocks are baked at a temperature of about 1200° to 1300° in a kiln, in principle resembling a pottery kiln, the surface of the blocks being protected from oxidation by being embedded in carbon. The permissible current-density for good electrodes of this type is in the neighbourhood of 8 amperes per square inch of transverse section. For further details and description of Mendheim and other kilns suitable for baking the blocks, reference may be made to Die Künstlichen Kohlen, by Julius Zellner. Also to Chem. and Met. Engineering, vol. xix. 179, where an illustration of a more modern type of kiln known as the Meiser Kiln is shown. Various types of tunnel furnaces are also in use for this purpose (and for baking pottery and bricks). The connection of the carbon blocks with the anode beam carrying the current may be effected by means of an iron claw let into the block or a copper hanger fitted into it by a screw contact or by other devices.

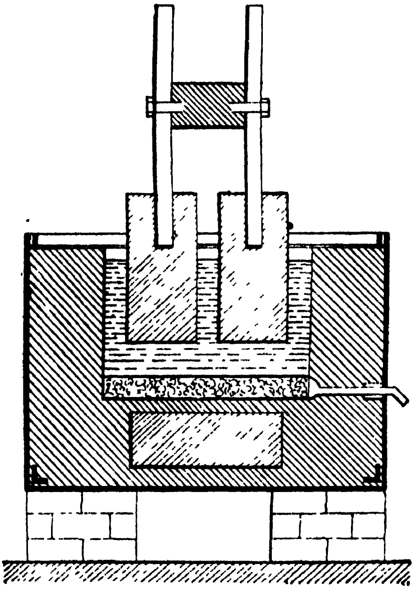
The Reduction Furnaces.—These consist essentially of an iron casing lined with carbon, the general character and arrangement of which is shown in transverse section below. The electrodes vary in size and form in different works, and are not necessarily arranged in two rows as indicated in the figure. Their total sectional area is, however, always adapted to the current to be used and good electrodes will act satisfactorily under a current-density of about 8 amperes to the square inch. The lower part of the carbon body serves as the cathode, or a special form of cathode is let into the carbon at the base of the furnace. In starting a furnace it is usual to introduce first the cryolite, which is brought to a state of fusion by electrical heating. Alumina is then fed in gradually at the surface of the cryolite, and as it dissolves the resistance gradually falls to about 5 or 6 volts, and the temperature of the bath will be generally 1000°. The electrolytic action brings about a decomposition, which has been usually taken to result in the formation of carbon monoxide, according to the equation

$$Al_2O_3 + 3C = 2Al + 3CO$$

but there is little doubt that primarily carbon dioxide is formed, and the change should be expressed as

$$2Al_2O_3 + 3C = 4Al + 3CO_2$$

In the former case the carbon used would be two-thirds of the weight of the aluminium produced, whilst in the latter it would be one-third. In practice the ratio of carbon to aluminium lies between these extremes.



The production of aluminium is discontinuous, for about 2 hours after the proper charge of alumina has been added the voltage of the furnace rises rapidly and affords an indication that more alumina must be added. The aluminium collects at the bottom of the bath of electrolyte, and is tapped off at stated periods, either every day or at longer intervals. The reduction of alumina by electrolytic methods on a laboratory scale is beset with difficulties; an account of experiences in this direction is given in papers by Neumann and Olsen (Met. and Chem. Engineering, 1910, 185), and Tucker (*ibid.* 1909, 315). The metal is subsequently re-melted and cast into notch bar slabs or blocks. The blocks are broken down in heavy rolls and further brought down into sheet. Metal which has been subject to much cold work in rolling is in a stressed condition. To render it homogeneous it is exposed to an annealing process at about 400°. The resulting sheet is ultimately obtained according to details of treatment in soft, medium, or hard condition. The metal may also be drawn into wire or extruded in large masses either in solid sections or in tube.

Physical Properties.—Commercial aluminium is a metal with the whiteness of tin. It has been obtained in crystals resembling octahedra, and is very slightly magnetic.

Its specific heat is, at

−100°	0·1893	300°	0·2434
0°	0·2098	500°	0·2739
100°	0·2236	650°	0·3200

(Schmitz, Proc. Roy. Soc. 72, 177).

The total heat required to bring a kilogramme of aluminium from 0° to 625° is 239,400 cals., and its latent heat of fusion is usually taken as 80 calories per gram. Laschtschenko (J. Chem. Soc. 1913, Abst. 427) found for metal of 99 p.c. purity the value 71. It melts at 654·5° (Heycock and Neville), 657·3° (Holborn and Day), the melting-point being dependent (as are other physical properties) on its purity. Small amounts of silicon and iron, which are always present, have a considerable effect on its behaviour, both physically and in contact with reagents. Lorenz found its conductivity for heat at 0° 0·3435, at 100° 0·3619; whilst Jaeger and Dresselhorst for metal containing 0·5 p.c. iron and 0·4 p.c. copper, found 0·4923 at 100°. Similarly the electrical conductivity of aluminium, taking copper as 100, is as follows: 98·5 p.c. purity, 55; 99 p.c., 59; 99·5 p.c., 61; specific resistance, 2·7–2·8 microhms increasing to 3·6 at 100°.

Its elasticity modulus (*i.e.* load in kilogrammes per square millimetre, divided by its alteration in length) is 7462 as compared with 11,350 for copper, and the torsion moduli of these metals are 3350 and 4450 respectively.

The specific gravity of the molten metal is 2·54, and of the cast metal is about 2·66; this may be increased by rolling. Its thermal expansion is given by the formula $l_t = l_0[1 + 22 \cdot 9t + 0 \cdot 009t^2)10^{-6}]$ (Jaeger and Scheel). It expands on fusion to the extent of 4·8 p.c. (Toepler). The metal expands in volume from 0°C. to melting point 6·1 p.c., after fusion reaches 10·9 p.c., and at 800° C. 12·4 p.c. In hardness it resembles silver, and the pure metal is softer than the impure. It becomes more elastic and also harder by hammering and rolling, and is capable of being drawn down to a wire of $\frac{1}{250}$ inch in thickness, or rolled into plate or beaten into foil to $\frac{1}{2500}$ inch thick. It can also be finely granulated, or prepared in the form of powder (Guillet, J. Soc. Chem. Ind. 1912, 339), which is largely employed as 'thermite,' or as aluminium paint. The tensile strength of aluminium is 12 to 13 tons on the square inch, but this varies with the temper of the metal between 6½ and 15½ tons on the square inch, the elongation varying in the inverse manner from 23 p.c. to 1½ p.c. 6-mm. wires have a tensile strength of 13 kg./mm.² and 3-mm. wires a strength of 17 kg./mm.². Aluminium has been largely used for overhead electrical transmission and it possesses many advantages for such purposes owing to its lightness. Its specific gravity being only $\frac{3}{10}$ of that of copper, and conductivity over 60 p.c., it follows that an aluminium cable has double the efficiency of a copper cable of the same weight as a means of conveying current. The tensile strength of aluminium is affected, of course, by its form, method of casting and mechanical treatment. Its ultimate strength in tons per square inch is in castings 5 tons, in sheet 8 to 9 tons, and in wire from 13 to 29 tons. On annealing its strength is reduced about 50 p.c. and its ductility much increased, the elongation being 4 to 8 times greater than when it is in the hard-rolled form.

Although corroded in the atmosphere of some large towns, it is not more so than other metals used for cables, and under ordinary circumstances it merely becomes coated with a thin film of oxide which acts protectively (Kershaw, J. Soc. Chem. Ind. 1901, 133; E. Wilson, J. Soc. Chem. Ind. 1902, 1283; 1903, 1093). A protective coating for insulation purposes can also be produced (Mott, J. Soc. Chem. Ind. 1904, 509; Skinner and Chubb, J. Soc. Chem. Ind. 1915, 360; also Eng. Pat. 9941, April 24, 1911).

There has been great difficulty in finding a wholly satisfactory solder for the metal, and one that shall resist corrosion. Dagger (J. Chem. Soc. Ind. 1891, 436) quotes as useful for heavy soldering Al 12 pts. Cu 8 pts. Zn 80 pts., and for light soldering Al 6 pts. Cu 4 pts. Zn 90 pts. A satisfactory flux for soldering consists of $NaCl$ 30 grams, KCl 45 grams, $LiCl$ 15 grams, KF 7 grams, $NaHSO_4$ 3 grams (J. du Four Electrique, 1914, 868). Joints can, however, be made by autogenous welding with an oxyhydrogen or acetylene flame or electrically. Butt and other joints may be effected by various mechanical devices with the aid of fusion at the surfaces or by a casting of metal around the junctions.

Applications of Aluminium in the Industries.—*Castings* or extrusions of the metal or its alloys are used in the construction of railroad cars, motor-cars, air-ships, and aeroplanes; for collector bows, field coils, and other details in electrical traction, also for various mechanical appliances, such as pulleys, &c. *Sheet* is largely employed for spinning, pressing, or stamping into forms suitable for cooking vessels, trays, drawers, beakers, and similar articles of domestic use, or in works operations. *Wire* and extruded metal is employed in the distribution of electrical current either by means of solid or stranded cable, for feeder connections or bus-bars. In America, on the Continent, and in Canada and other Colonies aluminium is used for overhead high-tension currents running to over 100,000 volts. In Great Britain its use is confined to lower-tension currents either over or underground.

Granules and Notch Bar are cast in this form for convenient addition to molten steel during casting with the object of securing greater purity and density of the steel. In the form of *powder*, or as finely *granulated* metal, aluminium finds application in the thermite welding process, as paint, and for the manufacture of high explosives, such as ammonal. In consequence of the very large number of chemical products which have practically no action upon aluminium, the metal is now being used with advantage in a large number of chemical industries. The following may be quoted as processes or branch industries, in which already wide applications in the construction of plant are being found for the metal:—

Manufacture of nitric acid and guncotton, &c.; oils, fats, soap, glycerine, organic acids; fine chemicals, such as formaldehyde, hydrogen peroxide, ether, extracts, essences, and syrups; foodstuffs, gelatin, jams, etc.

Also in the canning industry, sugar refining, varnish making, brewing, dyeing, rubber, paper, lithography, and printing.

Chemical Properties.—Aluminium absorbs about its own volume of hydrogen (Delachanal and Dumas, J. Soc. Chem. Ind. 1909, 368), which is, however, expelled on heating or *in vacuô*. In the course of its production and treatment aluminium takes up gases (chiefly hydrogen and nitrogen) usually in such quantity that their total volume is from 7 to 20 p.c. of that of the metal. Good metal tapped from the reduction furnaces yields 5 to 10 p.c. of its volume of hydrogen and about 3 to 4 p.c. of nitrogen. After re-melting, especially under unsuitable conditions, it is found to contain more hydrogen and also carbonic oxide and hydrocarbons. An ingot of metal, which had been melted and allowed to cool in the furnace *very* slowly, was highly crystalline and found to contain of its volume an extraordinary amount, viz. 85 p.c. hydrogen, 7·5 p.c. nitrogen, and 4 p.c. carbonic oxide and hydrocarbons. It is practically unacted upon by oxygen at ordinary temperatures, but if finely divided it undergoes considerable oxidation at 400°, or even, though less rapidly, at lower temperatures. If sufficiently pure, water has slight action upon it, though if sodium is present in the metal a somewhat greater action occurs. This is accentuated if copper, brass, or other metals are in contact with it. A recent use to which the metal has been put is for the treatment of hard waters, which by intimate contact with the metal, are said to be softened and become less liable to form incrustation on the shell of the boiler. The halogen elements or acids readily act upon aluminium, and the chemical activity of the metal is such that a large amount of heat is generated on combination with these elements.

The very great affinity which aluminium possesses for oxygen has been made use of in the application of 'thermite' as a means of reducing oxides. Goldschmidt, D. R. P. 96317 (1895), has thus used the finely divided metal in the production of iron, manganese, chromium, nickel, cobalt, titanium, boron, molybdenum, tungsten, vanadium, and other metals.

Reagents which readily part with the halogens, such as $SiCl_4$ and PCl_3, also attack it, and carbon or the oxides of carbon at high temperatures convert it into the carbide, Al_4C_3. Mallet (Chem. Soc. Trans. 1876, 340) found that molten aluminium is acted upon by nitrogen with the formation of nitride, indeed it burns vigorously in an atmosphere of nitrogen.

If brought into intimate contact with mercury in presence of moisture, aluminium is readily converted into the hydroxide, and when exposed to the vapour of mercury with access of air, it undergoes rapid oxidation.

Perspiration, being acid, has no apparent effect; saliva, on account of its slight alkalinity, acts very slowly. Aluminium tubes have been used for insertion in the human body where much purulent matter was present, without perceptible corrosion.

Aluminium when fused with potash or soda is unaffected even at a dull red heat, but the superficial silicon is removed; metal so treated takes a good 'matt.'

For burnishing and engraving aluminium, the ordinary media are unsuitable. According to Mourey and others, an emulsion of equal parts of rum and olive oil is most satisfactory. The finish of manufactured articles is improved by a frosted appearance. This is produced by plunging the article momentarily into caustic alkali, washing well, and immersing in dilute nitric acid.

Action on metallic solutions.—Aluminium, especially in the form of foil, has a considerable action on many salts in solution. The action of sulphates and nitrates is usually very slow. All chlorides, except those of the alkalis and alkaline earths, are readily decomposed, even *aluminium chloride* solution dissolves the metal with evolution of hydrogen. Bromides and iodides have corresponding effects. The presence of chlorides in solutions of other salts much facilitates their action.

From a neutral or feebly acid solution of silver nitrate, silver is precipitated slowly; from an ammoniacal solution of the chloride, silver is rapidly precipitated as a crystalline powder.

From the nitrate or sulphate of copper, precipitation is slow, from the acetate quicker, and from the chloride or other salt in presence of sodium chloride, rapid and complete.

Salts of mercury are decomposed with formation of an amalgam. Lead and zinc are readily precipitated (*v.* also Cossa, Zeitsch. f. Chem. [2] 6, 380 and 443; Nicolardot, J. Soc. Chem. Ind. 1912, 438).

Action of dry salts and oxides.—The action of aluminium, when heated with certain salts and oxides, is peculiar, and shows, especially at high temperatures, the tendency of this metal to form aluminates.

It is not affected by potassium nitrate except above a red heat; it is then rapidly oxidised with formation of potassium aluminate. With alkaline carbonates combination takes place at a red heat with separation of carbon, and with alkaline sulphate combination takes place suddenly at redness with explosive violence; in both cases aluminates are formed.

When finely divided aluminium is mixed with oxide of copper, lead, or iron, combination takes place at a *white* heat only, with such violence as frequently to shatter the crucible. In the case of lead and copper oxides, aluminates are produced, and with iron an alloy of iron and aluminium (Tissier).

When heated with silicates or borates, aluminium liberates silicon or boron, forming an aluminate with the base. Fused silver chloride is reduced to metal; zinc is reduced from its fused chloride, whilst magnesium chloride is not affected (Flavitzky, Ber. 6, 195). The vapour of mercuric chloride is reduced with such energy by heated aluminium that the metal fuses.

Corrosion of aluminium.—The question of corrosion is one which is of the highest importance in the application of metals, but in none more so than in the case of aluminium (Bailey, J. Inst. Metals, ix. 79, and xxi., 234).

This arises not only from the considerable extent of the usage of this metal for culinary operations, but also because of its large and extending use in the chemical industries and for constructional work where atmospheric and other agencies are to be reckoned with.

Speaking generally, with the exception of alkalis and salts with an alkaline reaction, solutions containing less than 5 p.c. of the reagent have very little action.

It is also noteworthy that concentrated mineral acids or organic acids, and with few exceptions the salts of these react very slowly with aluminium. The most important exceptions are hydrochloric acid and the halogen acids generally.

It is essential, however, to add that whilst this general statement holds good at ordinary temperatures, action is very greatly accelerated by a rise in temperature, and especially when the reagent approaches its point of ebullition. The extent to which aluminium is corroded is also largely dependent on its purity, especially where this is lower than that of good commercial metal, say 99·2 p.c., or, of course (though in practice this is frequently overlooked), aluminium is in contact with other metals. In the notes which follow, some information is given as to the corrosive effects of those reagents which are already associated with the use of aluminium in the industries, and references are given to details.

The numbers stated in parentheses, in respect of any of these reagents, express the milligrams of metal removed per 100 square centimetres of surface for an exposure at ordinary temperatures of 24 hours, when the concentration is approximately 5 p.c., except where otherwise stated.

Acetic acid (0·6) (Lunge, J. Soc. Chem. Ind. 1895, 592; Seligmann and Williams, J. Soc. Chem. Ind. 1916, 88, and 1917, 409).

Acetone (Pikes, Zeitsch. angew. Chem. 1914, 52).

Alcohol, wines, and *spirits* (Lunge, *l.c.*; Rüdiger and Karpinski, J. Soc. Chem. Ind. 1913, 41).

Ammonium hydroxide (reaches maximum with 2 p.c. at 375) (E. K. Davis, Metal. Ind. 1910, 109).

Barium hydroxide (370 for centinormal solutions).

Beer (Schönfeld and Himmelfarb, J. Soc. Chem. Ind. 1912, 789; Chapman, *l.c.* 1912, 87; Bleisch, *l.c.* 1912, 199; Zikes, *l.c.* 1913, 248; Trillat, *l.c.* 1915, 883).

Boric acid (0·3) (Lunge, *l.c.*).

Bromine acts vigorously on aluminium, also *chlorine* and *iodine*.

Butyric acid (0·2) (Lunge, *l.c.*; Seligmann and Williams, *l.c.*).

Calcium hydroxide (285 for a centinormal solution).

Citric acid (0·3) (Lunge, *l.c.*).

Formic acid (Seligmann and Williams, *l.c.*).

Hydrochloric acid (7).

Lactic acid (0·8) (Lunge, *l.c.*).

Nitric acid (5) (Seligmann and Williams, J. Soc. Chem. Ind. 1916, 665).

Oxalic acid (6) (Carpenter and Edwards, 9th Report of Alloys Research Committee).

Potassium hydroxide (205 for a centinormal solution).

Potassium iodide (1·3).

Propionic acid (Seligmann and Williams, J. Soc. Chem. Ind. 1916, 88).

Salicylic acid (1·1) (Lunge, *l.c.*).

Sodium chloride (2).

Sea water (13) (Carpenter and Edwards, *l.c.*).

Sodium hydroxide (460 for a centinormal solution).

Sodium carbonate (reaches maximum with 0·5 p.c. at 140).

Sodium bicarbonate (little or no action).

Sulphuric acid (7).

Tartaric acid (0·3) (Lunge, *l.c.*).

It should be realised that corrosion measured, especially in the cold and over short exposures, shows in many cases, a much higher value than would be the case for prolonged exposure, owing to the formation of a protective coating. This applies particularly to weathering, action of ammonia, and certain hydrates and salts, and more commonly in hot solutions.

With the fixed alkalis the activity is progressive with increased concentration, and also in a very rapid degree with hydrochloric acid; but with ammonia, sodium carbonate, and with sulphuric, nitric, and acetic acid the activity rises to a maximum, and ultimately falls off rapidly, so that with the highest concentration the action is slight. Many of the results given above have been confirmed by the author of this article or are the results of unpublished determinations by him. It only remains to add that the following bodies have practically no action on aluminium: Acetone; acetylene; benzol; tea and other similar beverages; borax; chlorides; sulphates and nitrates of the alkalis; carbolic acid; ether; fats, oils, and fatty acids; formaldehyde; gallic acid; gelatin; glycerine; hydrogen peroxide; hydrogen sulphide; soap; sulphur; sulphur dioxide; chlorine.

Potable waters, if free from common salt and alkalis, have very slight effect.

Detection.—Compounds of aluminium, when heated, moistened with solution of cobalt nitrate, and again strongly heated produce a fine sky-blue colour (*Thenard's blue*, *q.v.*, art. COBALT).

Aluminium compounds are usually colourless. Silicates and other compounds insoluble in acids require to be finely powdered, mixed with 4 parts of sodium carbonate or fusion mixture, and heated strongly in a platinum crucible The aluminium, having thus become converted into sodium aluminate, is dissolved out with hydrochloric acid, evaporated to dryness to render any dissolved silica insoluble, and treated with dilute hydrochloric acid. The aluminium is then present as chloride.

Aluminous solutions, on addition of an alkali, give a white gelatinous precipitate of hydrate, soluble in excess of the precipitant and in acids. Ammonia produces the same precipitate, which is only slightly soluble in excess, and is entirely reprecipitated on boiling off the excess of ammonia if sufficient ammonium chloride be present, or it may be precipitated by CO_2.

Estimation.—Aluminium is usually precipitated as the hydrated oxide $Al_2O_3,3H_2O$.

For this purpose the solution, which, in presence of alkalis or alkaline earths, is mixed with excess of ammonium chloride, is treated with a *slight* excess of ammonia, and the solution boiled until the free ammonia is expelled. The hydrate, having thus become totally precipitated, is filtered, well washed, dried and heated in a platinum crucible, the heat being finally raised to bright redness to constant weight over the blowpipe. The weighed residue consists of anhydrous oxide, Al_2O_3, and contains 53 p.c. of aluminium. The separation from other metals is not difficult. The heavy metals may be precipitated from the *acid* solution by sulphuretted hydrogen, leaving the aluminium in solution, whilst the precipitation in presence of ammonium chloride in excess separates it from the alkalis and alkaline earths. From chromium and iron the separation is less simple. Chromium may be separated as follows:—The precipitated oxides are dried, mixed with 2 parts potassium nitrate and 4 sodium carbonate and fused in a platinum crucible. Alkaline chromate and aluminate are thus produced. The mass is digested with water and a small quantity of potassium chlorate and of hydrochloric acid are then added, and the solution is evaporated to a syrup, with occasional addition of potassium chlorate to destroy the excess of hydrochloric acid and prevent its reducing action on the chromate. The aluminium in the diluted solution is precipitated as above by ammonia, leaving the chromate in solution.

For the separation from iron, the precipitated hydrated oxides are dissolved in the minimum quantity of hydrochloric acid and treated with an excess of *pure* strong potassium hydroxide solution, boiled for a few minutes, diluted, filtered, and well washed. The ferric oxide is thus precipitated and separated from the soluble alumina. The solution and washings are acidified with hydrochloric acid and precipitated by ammonia. On account of its solvent action upon glass, the treatment with potash should be performed in a porcelain dish, which is much less attacked, or, preferably, in one of silver.

Commercial Analysis of Aluminium.—The direct determination of aluminium, constituting as it does usually over 99 p.c. of the metal under examination, presents many difficulties. It has been proposed to estimate the aluminium by ascertaining the volume of hydrogen evolved on dissolving it in hydrochloric acid or the amount of chloride formed, but the errors to which such a determination is liable are too great to admit of sufficient accuracy; moreover, the impurities usually present give rise to corrections which detract from the simplicity of the method and complicate the result. The solution in caustic soda is preferable to this, the iron and copper remaining as a black residue, but the silicon, in part, at least, reacts with caustic soda, so that even in this case the hydrogen evolved cannot be taken as a measure of the aluminium present. In these circumstances it is customary to determine the impurities and arrive at the amount of aluminium by difference.

The impurities generally present in quantity are iron, silicon, and sometimes copper. Minute amounts of sodium, carbon, and nitrogen are also contained in the metal, but these should not greatly affect the result unless when dealing with specially impure metal. Commercially, therefore, iron and silicon alone are usually estimated. For the *iron*, the metal is dissolved in caustic soda, and this solution on acidulation with sulphuric acid yields sulphates of alumina and iron which redissolve in the acid, whilst the presence of copper is indicated by the appearance of a black residue. The amount of iron is finally determined by titration with potassium permanganate. For the *silicon*, the metal is digested with hydrochloric acid in presence of nitric acid (to avoid volatilisation of any silicon as chloride) forming a turbid solution owing to the separation of the silica. This is then boiled down with sulphuric acid until white fumes of this acid appear. The aluminium and iron salts are thus converted into sulphate, and redissolve on digestion with water, the silica being left in suspension.

After filtration and washing, the silica is strongly heated and weighed. *Copper* may be estimated as sulphide, or the black residue above mentioned may be dissolved and the copper estimated colorimetrically. If the amount of *sodium* is to be found, the metal must be dissolved in nitric acid, boiling acid of 60 p.c. strength being used. The solution is boiled down to dryness and exposed to a dull red heat so long as red fumes appear. The residue is extracted with water, care being taken finally to remove all alumina or other metals precipitated by the ordinary reagents. Ultimately the sodium salt remaining may be converted into sulphate and weighed as such. For fuller details a paper by Seligmann and Willott may be consulted (Journ. Inst. Metals, vol. iii. p. 138).

For general analytical details, the following sources of information may be consulted: Moissan (Compt. rend. 121, 851); Gouthière (Analyst, 21, 270); Jean (Rev. Chim. Indust. 8, 5); Withey (Journ. Inst. Metals, xv. 207). The better qualities of commercial metal should not contain more than 0·5 p.c. of iron and silicon together, nor more than 0·05 p.c. of sodium. It is, however, very doubtful whether sodium is present in the metallic form.

Alloys.—The addition of quite small quantities of aluminium to certain metals (*e.g.* copper and iron) has a profound effect in modifying the properties of these metals. Likewise the addition of small quantities of certain metals (*e.g.* Fe, Mn, Si, &c.) to aluminium effects considerable change in the properties of this metal. The addition of 0·1 p.c. of aluminium to copper brings down its conductivity 23 p.c.; the addition of zinc, copper, nickel, iron, or manganese to aluminium is accompanied by considerable augmentation of the tensile strength. The alloys of aluminium may be classified into bronzes, casting alloys, and rolling alloys, according to their properties. The *true bronzes* consist of copper and aluminium alone, but there are many binary (and ternary) alloys which contain metals other than copper and yet sufficiently resemble bronze to be classed along with it. The bronzes proper chiefly employed are gold bronze, containing 3 to 5 p.c. of aluminium; steel bronze, with 8·5 p.c. Al and some silicon; acid bronze, with 10 p.c. Al. The copper bronzes, with 90, 92·5, 95 and 97·5 p.c. of copper, are all good alloys, showing homogeneity and freedom from crystallisation. They are of great hardness and high tensile strength.

Such alloys possess very valuable properties, the ultimate stress of the 90 p.c. alloy being 38 tons to the sq. inch, and they have the further valuable property of being practically noncorrodible by sea-water; this property is also shown very markedly by bronzes containing manganese. These bronzes in hardness and tensile strength compare favourably with the best steel, and are similarly affected by tempering. The alloys high in aluminium and low in copper are also of great commercial value; a bronze with 4 p.c. copper by rolling and drawing showed a steady increase in tensile strength from 9·6 tons to 20 tons to the sq. inch.

A small percentage of manganese increases the tensile strength of aluminium without affecting its ductility, but large proportions of manganese increase the strength and lessen the ductility.

For further information reference may be made to the eighth report of the Alloys Research Committee of the Inst. Mech. Engineers (Carpenter and Edwards), and to the ninth report (Rosenhain and Lantsberry), and tenth report (Rosenhain and Archbutt), also to The Metal Industry, 1909, 186 (Hiorns); Schirmeister, J. Soc. Chem. Ind. 1916, 894; also J. du Four Electrique, 1914, 700. The composition of other bronzes used industrially is given in the following table:—

	Al	Cu	Zn	Sn	Ni	Cr	Mg
Hercules bronze .	2	65	33	—	—	—	—
Chromium bronze .	95·75	4	—	—	—	0·25	—
Duralum .	79	10*	—	—	—	—	11
Partinium .	88·7	6·8	4·5	—	—	—	—
Grossmann's alloy . .	87	8	—	5	—	—	—
Argentan .	7	70	—	—	23	—	—
Hercules metal (No. 3)	1·5	61	37·5	—	—	—	—

* Phosphorised copper.

The aluminium alloy containing 20–50 p.c. of copper or nickel is brittle, as is the alloy with 35 p.c. of manganese.

Rolling Alloys.—Aluminium alloys, containing 3 to 4 p.c. of copper or 1·5 to 5 p.c. of nickel, roll well, as do many other alloys containing copper and zinc, the former in small quantity, amounting to from 1 to 3 p.c., and the latter 10 to 12 p.c., or even more.

Magnalium consists of aluminium alloyed with 2 to 10 p.c. of magnesium. This alloy is lighter than aluminium, and in strength and workability equal to good brass. *Duralumin* is a very important alloy containing 3·5 to 5·5 p.c. Cu, 0·5 to 0·8 p.c. of Mn, and 0·5 p.c. Mg. An account of this alloy is to be found in the discussion on Tenth Report of the Alloys Research Committee; also Met. Industry, 1910, 393 and 413; and Met. and Chem. Eng. 1910, 547.

Casting alloys are also largely used, consisting most frequently of aluminium, zinc, and copper in varying proportions (Richards, Eng. and Mining Journ. 1908, 715). Magnalium admits of introduction with advantage of small quantities of copper and nickel without unduly raising its specific gravity. The tensile strength and hardness of these alloys are considerable, and they are said to be resistant to atmospheric corrosion (Barnett, J. Soc. Chem. Ind. 1905, 832). Taps, tuyères, and the like are made from an alloy composed of aluminium, to which 12 p.c. Cd, 6 p.c. Cu, 5 p.c. Sn, 2 p.c. Ni are added. Pedestals are also made of aluminium, containing 14 p.c. Sb, 1·2 p.c. Cu, 12 p.c. Sn, 37 p.c. Zn, and 0·8 p.c. Pb; copper, with 10 p.c. Al and 1 p.c. Mn, is an excellent hard alloy for bearing metal or tool steel; horse-shoes are made from a ternary alloy of aluminium containing either 12 p.c. Cu and 10 p.c. Zn, or 5 p.c. Cu and 10 p.c. Sn. Many alloys of aluminium resist acid corrosion to a remarkable degree, and even if cooking utensils are made from an aluminium copper alloy, Carpenter and Edwards have shown that when corrosion does occur the copper is not dissolved out, and hence there is no danger of poisoning in using such vessels, since the salts of aluminium have no toxic action.

An improvement is effected by the addition of aluminium to *brass*. An alloy containing aluminium 2·5 p.c., copper 70 p.c., and zinc 27·5 p.c., is said to show nearly double the tenacity and considerably more than double the elongation of ordinary cast brass.

The presence of *tin* in aluminium renders it more fusible and brittle. According to Bourbouze (Compt. rend. 102, 1317), an alloy of aluminium 100 and tin 10 is strong, easily worked, may be soldered as easily as brass, is whiter and less affected by reagents than aluminium, and is very suitable for parts of optical instruments. Its sp.gr. is 2·85. The addition of aluminium to tin increases its hardness and tenacity. The alloys containing 5, 7, and 9 p.c. of aluminium are all easily worked and soldered. A larger proportion of aluminium is liable to separate out on melting.

Aluminium combines in all proportions with *cadmium*, forming malleable fusible alloys.

Small quantities of *silver* increase the hardness and elasticity and lower the melting-point without rendering aluminium brittle. The alloy containing 4 p.c. silver has been used for the beams of delicate chemical balances. When the addition exceeds 5 or 6 p.c. the metal becomes brittle; the 50 p.c. alloy is as hard as bronze, but very brittle. '*Tiers argent*' consists of 1 part silver and 2 parts aluminium; it is of considerable hardness, and is used for table-spoons, &c. The addition of 5 p.c. of aluminium to silver renders it as hard as standard silver and very permanent.

The presence of aluminium in *gold* considerably alters its properties. The addition of 0·186 p.c. of aluminium to *pure* gold increases the tensile strength from 7 tons to 8·87 tons per square inch, a greater increase than is produced by the same amount of any other metal (Roberts-Austen, Roy. Soc. Rep. April, 1888; Chem. News, 1888, v. 57, p. 133). With 1 p.c. aluminium the gold has the colour of 'green gold,' is hard but easy to work; with 5 p.c. aluminium it is white and extremely brittle, and with 10 p.c. white, brittle, and crystalline. Aluminium containing 10 p.c. of gold is white and hard.

The malleability of aluminium is not much impaired by the addition of gold, silver, or tin, but the presence of excessive amounts of iron, and especially of silicon, is very injurious.

The alloys of aluminium and *silicon* appear to form a simple eutectiferous series, the silicon branch of the curve exhibiting no singularity whatever (Fraenkel, Zeitsch. anorg. Chem. 1908, 58, 154). These results have been confirmed by Roberts (Chem. Soc. Trans. 1914, 105, 1383). That no compound is formed is supported by the fact that no silicon hydride can be detected when the alloys are dissolved in acids; the silicon, as appears from a microscopic study of the structure of the alloys, crystallises in plates arranged in five- or six-rayed stars.

The presence of silicon renders aluminium brittle and much less permanent.

With *iron* the alloys are of especial interest. The presence of a quantity of iron is very injurious; it renders the aluminium crystalline, and raises the melting-point. The alloy containing 5 p.c. of iron is hard and brittle; with 8 p.c. the alloy crystallises in needles, and on heating separates into a more liquid alloy containing but little iron and a skeleton very rich in that metal. Michel (Annalen, 115, 102) has prepared an alloy which crystallises in six-sided prisms, corresponding to Al_2Fe. A beautifully crystalline substance having the composition Al_4Fe is often found in the neighbourhood of the cathode of a reduction furnace.

The valuable properties imparted to iron and steel by the presence of a small quantity of aluminium have long been known; Faraday (Quarterly Journ. Roy. Inst. 1819, 290) found from 0·013 to 0·069 p.c. of aluminium in certain samples of Bombay wootz, though it has been shown by Henry and others that this metal is not always present. About the same time S. B. Rogers showed the presence of aluminium in some of the best quality of pig-iron made in South Wales, and found that a steel to which 0·8 p.c. of aluminium had been added in the form of an alloy with iron, was rendered harder and stronger and resembled the best wootz (Rogers, Metallurgy, 1858, 14). A superior steel was prepared by Sir Charles Knowles, which was stated to owe its value to the use of *kaolin* and consequent introduction of aluminium into the metal in its preparation (Mining Journal, 1859, 118).

Messrs. Cowles Bros. have exhibited a Siemens-Martin basic steel containing 0·2 p.c. aluminium, which welds with iron and shows no mark at the junction.

The addition of aluminium to iron or steel for the production of 'mitis castings' has been patented by P. Ostberg (Engineering, 1886, 360). Iron and steel, especially at temperatures far above the melting-point, absorb considerable quantities of gas, which impairs the value of the castings. The addition of 0·05 or 0·1 p.c. of aluminium to the fused iron or steel lowers the melting-point, prevents the absorption of gas, and considerably increases the fluidity. The metal can then be easily cast.

Nickel and aluminium combine with incandescence when heated together. The presence of under 3 p.c. of nickel lowers the melting-point and increases the hardness and elasticity.

Pure aluminium combines with mercury, although not readily, when the metals are heated together in an inert gas such as carbonic anhydride. The two metals combine rapidly in presence of alkalis. The amalgam may also be produced by electrolysis of mercuric nitrate, using a negative plate of aluminium dipping in mercury. When aluminium is rubbed with wash leather impregnated with mercury, combination occurs; the surface rapidly oxidises and becomes heated, with formation of concretions of alumina (Jehn and Hinze, Ber. 7, 1498).

Alloys of *bismuth* with aluminium are hard and brittle. With *antimony* and *lead* aluminium does not unite, although traces of lead are frequently present in commercial aluminium.

Sodium unites readily with aluminium. The last traces of sodium are difficult to remove, especially, it is said, when the metal has been reduced from cryolite. The alloys are easily attacked by moisture, and burn in the air, with oxidation both of the aluminium and sodium; that containing 2 p.c. of sodium decomposes water with ease. The necessity of avoiding the presence of sodium in the preparation of aluminium is therefore obvious.

Aluminium also unites with *manganese*; with *platinum* it unites easily, forming fusible alloys. With *boron* aluminium combines in varying proportions. The so-called 'adamantine' and 'graphitic' boron appear to be borides of aluminium (Hampe, Annalen, 1876, 75; and Deville and Wöhler, *ibid.* 1867, 268) (*v.* BORON).

Mallet (Chem. Soc. Trans. 1876, ii. 350) has prepared a nitride of aluminium in small crystals hard enough to scratch glass. It may be obtained in colourless hexagonal needles of the composition AlN by direct union of its elements at 820°. It forms ammonia when fused with potassium hydroxide, or by heating with sulphuric acid. Alcohol forms triethylamine at 230°. Fichter and Spengel (Zeitsch. anorg. Chem. 1913, 82, 192). It dissociates in nitrogen at atmospheric pressure at about 1850°. When heated in nitrogen at a pressure of 4·3 atmos. it melts at 2150°–2200° (Wolff, Zeitsch. anorg. Chem. 1914, 87, 120).

For further information, *see* J. W. Richards, Aluminium and its Alloys, London.

Aluminium oxide, *Alumina*, Al_2O_3.

Aluminium forms only one oxide, Al_2O_3, corresponding to and isomorphous with the sesquioxides of iron and chromium.

This oxide occurs native, colourless as *hyaline, corundum*; or coloured by metallic oxides, as *ruby, sapphire, oriental topaz*, &c. (*q.v.*). Very impure, dark, and usually associated with magnetite and *hæmatite*, it occurs in large boulders in many districts, and is used as a grinding and polishing material in the form of *emery* (*q.v.*). The native oxide crystallises in the rhombohedral system; in hardness it comes next to the diamond. The finely coloured specimens are used as gems. It occurs almost pure in considerable quantities in the Alleghanies in Northern Georgia.

It may be prepared by the ignition of aluminium foil in air or oxygen; the oxide so produced is fused and as hard as corundum.

Alundum is fused alumina, a product made up into electrical furnace cores, crucibles, bricks and tubes where high refractory properties are of value. It withstands 2000°, and has a linear expansion of 0·0000078, a specific heat of 0·195; at high temperatures (over 1500°) it has a low electrical resistance. It is, however, inapplicable to use in some directions owing to its porosity.

Amorphous alumina may be produced by ignition of the precipitated hydrate, pure aluminium sulphate or ammonia alum; in either case alumina alone is left.

It is white and soft, but becomes hard on strong ignition. According to H. Rose (Pogg. Ann. 74, 430) the sp.gr. of the oxide after heating over a spirit-lamp is 3·725; its density may be raised to 4, just about that of corundum by heating in a porcelain furnace, but it still remains amorphous. It is remarkable that though the density of the artificially prepared alumina is nearly 4, its bulk density may be less than one-fifth of this. With a somewhat lower density the bulk density is higher, but is still such that it occupies a larger bulk than the same weight of water.

When heated by the oxyhydrogen blow-pipe, alumina melts at 2050° and crystallises; the addition of chromium oxide or a chromate imparts a ruby colour to the crystals.

Fremy and Verneuil (Compt. rend. 1888, 566) have prepared artificial rubies by heating to redness a mixture of barium fluoride and alumina containing a trace of potassium dichromate. The heat requires careful management. Fine rubies are thus formed in a friable matrix which may be separated by agitation with water. By former methods the matrix was hard and difficult to remove (Fremy and Feil, Compt. rend. 1877, 1029, and 1887, 737). The crystals contain no barium, easily scratch the topaz, and possess the form and properties of natural rubies; their crystalline form has been determined by Descloiseaux (Compt. rend. 1888, 567). By the addition of a little cobalt oxide before the fusion, sapphires may be produced.

Alumina is soluble, when strongly heated, in boric acid; the latter may be driven off at a very high temperature, leaving crystalline alumina. By the addition of the proper oxide the corresponding spinels may be produced, coloured by cobalt oxide (blue), chromium oxide (red), iron oxide (black), (Ebelmen, Ann. Chim. Phys. 3, 22, 211 and 33, 34). Only two *hydroxides* of aluminium are known, viz.: Al_2O_3,H_2O and $Al_2O_3,3H_2O$. By Graham's method an aqueous solution of the hydroxide may be obtained.

When the hydroxide is freshly precipitated it dissolves readily in dilute acids, but on standing, or after filtration, solution is more difficult, and is best achieved by a mixture of 8 parts of sulphuric acid and 3 parts of water. When heated, the hydroxide loses its water, undergoing a contraction of about 30 p.c. in bulk as it passes into the form of the anhydrous oxide.

When boiled with water containing a drop of a 1 p.c. solution of alizarin, the hydroxide assumes a bright red colour, not removed by a weak solution of acetic acid.

This test easily distinguishes it from gelatinous silica. Aluminium hydroxide possesses a powerful affinity for many organic substances, and enters into association with a large number of colouring matters, precipitating them entirely as *lakes*. On this property depends the use of alum mordants (red liquor, &c.). They precipitate the hydroxide upon the fibre of the goods to be dyed, and this constitutes the *mordant* or fixing agent which retains the colour.

Sodium aluminate $Al_2O_3 \cdot 3Na_2O$ or $Al_2(NaO)_6$. This salt is now prepared on a large scale, both to be used as such and as an intermediate product in the preparation of the sulphate and other salts of aluminium.

Its formation depends upon the property possessed by alumina of acting as an acid in presence of a powerful base.

Its preparation from bauxite has already been described It may also be produced by passing a current of steam through a heated mixture of bauxite and common salt, and by strongly heating a mixture of bauxite, sodium sulphate, and carbon, but in the latter case its purification from the sodium sulphide simultaneously produced is difficult. It is also formed in the preparation of soda from *cryolite*. According to Thomsen's method, powdered cryolite is heated to redness with chalk, forming sodium aluminate and calcium fluoride :—

$$Al_2F_6 \cdot 6NaF+6CaCO_3=Al_2(NaO)_6+6CaF_2+6CO_2$$

The mass produced is lixiviated with water and filtered. From this aluminate the hydroxide is precipitated by carbon dioxide with formation of sodium carbonate :—

$$Al_2(NaO)_6+3CO_2+3H_2O=Al_2(OH)_6+3Na_2CO_3.$$

The hydroxide is usually made into aluminium sulphate by solution in sulphuric acid, or it is converted into alum.

An entirely different process has been introduced by Sauerwein. The finely powdered cryolite is boiled with milk of lime forming aluminate as before :—

$$Al_2F_6 \cdot 6NaF+6CaO=Al_2(NaO)_6+6CaF_2.$$

For the conversion of the aluminate into oxide Sauerwein applies a peculiar property possessed by that salt, which shows the readiness with which alumina loses its acid properties and again becomes basic. Sodium aluminate, when mixed in equivalent proportions with any haloid salt of aluminium, is decomposed ; the sodium combines with the halogen, while the whole of the aluminium is precipitated as hydroxide. On the large scale the haloid salt used is cryolite. The finely powdered mineral is stirred into the clear liquid from the previous operation, and the alumina precipitated as hydroxide :—

$$Al_2(NaO)_6+Al_2F_6 \cdot 6NaF+6H_2O$$
$$=2Al_2(OH)_6+12NaF.$$

Sodium aluminate is a white, infusible, amorphous solid, easily soluble in both cold and hot water. The concentrated solution rapidly deposits alumina, leaving in solution a basic aluminate, which on evaporation is obtained as a fusible and hygroscopic mass. The addition of any acid at once decomposes it with precipitation of alumina. This alumina is pure and free from alkali, which is never the case when alkaline precipitants have been used. It may be employed as a mordant in dyeing and calico-printing, in an acid and not, as in the case of alum, an alkaline bath. For the production of *lakes* the colouring matter is mixed with the aluminate solution and precipitated by the addition of sulphuric acid. According to Morin these lakes are richer than those obtained from alum and are produced at about one half the cost.

Potassium aluminate $Al_2O_3 \cdot 3K_2O$ or $Al_2(KO)_6$ is obtained in hard glistening crystals when alumina is fused with potash, the mass boiled in water and the solution evaporated *in vacuô*.

Aluminium chloride Al_2Cl_6. This compound was first prepared in 1824 by Oersted, by passing chlorine over a mixture of alumina and charcoal heated to redness. The method and apparatus resemble that used in the preparation of the double chloride, omitting the sodium chloride.

According to P. Curie (Chem. News, 28, 307) it may be easily prepared as follows :—Anhydrous alumina, or, less satisfactorily, clay, is strongly heated in a tube and subjected to a current of hydrochloric acid impregnated with carbon disulphide by bubbling through that liquid. Aluminium sulphide appears to be formed and at once decomposed by the hydrochloric acid, yielding aluminium chloride and sulphuretted hydrogen. The condensed chloride may be freed from sulphur by distillation with iron filings.

A solution of the chloride may be obtained by dissolving the hydroxide in hydrochloric acid.

The pure anhydrous chloride is a white, waxy, crystalline solid ; in presence of a trace of iron it becomes yellowish. On heating, it volatilises without fusion. If large pieces be quickly heated they fuse and boil at 180° to 185° (Liebig). It is very hygroscopic, and evolves hydrochloric acid on exposure to the air ; is easily soluble in water ; soluble in alcohol and ether. When deposited from a solution in hydrochloric acid, it forms crystals of the formula $Al_2Cl_6,12H_2O$.

It absorbs ammonia and combines with many metallic chlorides, forming double chlorides, the most important being that with sodium. Aluminium chloride has been recommended by Filsinger (Chem. Zentr. 10, 1270) for the preservation of wood, and by Saget (Chem. News. 45, 113) and others (J. Soc. Chem. Ind. 1882, 185 and 230) for the production of a discharge on indigo blue. An impure chloride containing calcium and sodium salts is stated to be largely used as a disinfectant under the name 'Chloralum.'

Double chloride of aluminium and sodium $Al_2Cl_6,2NaCl$. This compound may be produced by fusing together the proper proportions of aluminium and sodium chlorides. It is a colourless crystalline solid, melting at 185° (Deville) and volatilising at a red heat. It is slightly hygroscopic, but much less so than aluminium chloride ; it is also more stable and more satisfactory in use than that substance, and gives up nearly the whole of its aluminium when reduced by sodium.

Aluminium bromide Al_2Br_6 is most readily prepared by the action of bromine on metallic aluminium. The action is violent, and the metal should only be added gradually. A lump of aluminium weighing twenty grams becomes strongly heated and even fused on being placed in cold bromine (Mallet, Phil. Trans. 171, 1018).

It may also be prepared by the action of bromine on a strongly heated mixture of alumina and carbon, and, in solution, by dissolving the hydroxide in hydrobromic acid. It crystallises in colourless shining laminæ, which melt at 93° (Deville and Troost) and boil at 263·3° (at 747 mm.) (Mallet).

Like the chloride, it forms a double bromide, $Al_2Br_6,2KBr$.

Aluminium iodide Al_2I_6 may be prepared by heating aluminium with iodine in a closed tube. It melts at about 185° (Weber) and boils at 350° (Deville and Troost); its vapour is combustible. It dissolves in water, alcohol, and carbon disulphide.

Aluminium fluoride Al_2F_6, may be prepared by the action of gaseous silicon fluoride, or of hydrofluoric acid upon aluminium. It forms transparent rhombohedra, volatile at a red heat, insoluble in water and unacted upon by acids. In solution in hydrofluoric acid, it appears to form the compound $Al_2F_6{\cdot}6HF$, the acid corresponding to the double fluoride of aluminium and sodium.

Cryolite $Al_2F_6{\cdot}6NaF$. This important compound may be prepared artificially, and attempts have been made to produce it as a substitute for the natural cryolite, it being claimed that the artificial cryolite possesses the advantage of being lighter and melting at a lower temperature (J. Soc. Chem. Ind. 1890, 945). In recent years, however, artificial cryolite has been put on the market which presents no essential difference either in composition or properties from natural cryolite. Natural cryolite occurs in quantity only in one locality, in a large vein in the gneiss at Ivigtut in Greenland. Greenland cryolite has the following composition: Al 13·2, Na 32·7, F 54·2, and small quantities of silica. The melting-point of mixtures of cryolite and alumina is said to be—

Cryolite	1000°
With 3 p.c. Al_2O_3 . .	974°
,, 6 p.c. ,, . .	960°
,, 10 p.c. ,, . .	980°
,, 15 p.c. ,, . .	994°
,, 20 p.c. ,, . .	1015°

(Chem. Soc. Abst. 1907, 469; also Chem. Soc. Abst. 1913, 508).

It is a semi-transparent, white, crystalline, brittle solid, which melts at the edges in a candle flame. Its hardness is 2·5 to 3; its sp.gr. 2·95, but 2·21 in the fused state. When impure it is frequently yellowish-red or even black (*v.* CRYOLITE).

Cryolite is used as a flux in the manufacture of aluminium; formerly for making salts of sodium and aluminium; and for the manufacture of an opaque, porcelain-like glass. It is also used for enamelling pans and as a glaze for pots as replacing lead glaze. (*See* further, Benzon, Hoffmann's Ber. Entw. Chem. Ind. [1] 660).)

Aluminium sulphide Al_2S_3, may be prepared by strongly heating a mixture of aluminium and sulphur, or by heating alumina to bright redness in the vapour of carbon disulphide. It forms a yellow, glassy mass, which fuses at 1100°, and burns in air with production of alumina and sulphur dioxide. It may be purified by sublimation in a vacuum at 1100°–1250°, and then forms white needles resembling asbestos of sp.gr. 2·02 13°/13° (Biltz and Caspari, Zeitsch. anorg. Chem. 1911, 71, 182). It is readily hydrolysed by water. Houdard (Compt. rend. 1907, 801) found that by heating aluminium turnings and sulphides of manganese iron and chromium in a carbon boat, sulphides related to the spinels are formed, of which he prepared

$$MnS,Al_2S_3,\ FeS,Al_2S_3,\ CrS,Al_2S_3$$

Aluminium carbide Al_4C_3 may be obtained by the action of carbon or the oxides of carbon on alumina at very high temperatures, and often occurs in small quantity contaminated with nitride in the neighbourhood of the cathode of aluminium reduction furnaces in the form of a yellow powder; it is formed when a mixture of alumina and carbon is submitted to a current of 300 amperes at 65 volts. It possesses the remarkable property of being stable at high temperatures, and yet undergoing decomposition at a dull red heat. It reacts, though somewhat slowly, with water or dilute acids with the production of methane. The formation of carbide and ultimately its decomposition has been proposed as a means of preparing alumina from clay or other crude materials. Pring (Chem. Soc. Trans. 1905, 1530) found that up to 1400° C. the carbide acts as a reducing agent on metallic oxides,

$$Al_4C_3+12MO=2Al_2O_3+3CO_2+12M$$

but at higher temperatures alloys of aluminium and the metal are produced, only carbon being oxidised,

$$Al_4C_3+3CuO=Al_4Cu_3+3CO$$

owing to the fact that alumina can be reduced by carbon at very high temperatures; at lower temperatures the aluminium is oxidised by carbonic oxide as observed by Moissan,

$$6Al+3CO=Al_4C_3+Al_2O_3$$

the reaction being reversed at the higher temperatures.

Aluminium sulphate $Al_2O_3(SO_3)_3,18H_2O$ or $Al_2(SO_4)_3,18H_2O$. Aluminium sulphate occurs naturally in considerable quantities. As the hydrated salt of the above composition, it forms the chief constituent of the mineral *alunogen, halotrichite, feather alum,* or *hair salt,* which is found in volcanic districts, at Bilin in Bohemia, Copiapo in Chile, &c. It also occurs in pyritic shale. A sample of feather alum from Friesdorf, Bonn, was found by Rose to contain Al_2O_3 14·9 p.c., SO_3 37·4 p.c., FeO 2·5 p.c., H_2O 45·2 p.c., with traces of K, Na, Mg, and SiO_2.

Aluminite or websterite, a hydrated basic salt of the composition $Al_2O_3SO_3,9H_2O$, has been found at Auteuil, Halle, Muhlhausen, &c.

In combination with potassium sulphate, the basic salt occurs also in *alunite, alumstone,* or *alum rock* $K_2SO_4,3Al_2O_3(SO_3),6H_2O$, a mineral which is found in large quantities at La Tolfa near Civita Vecchia, in Hungary, at Puy-de-Sancy and Madriat in Auvergne, New South Wales, Kyoquot Sound (Canada), and in many other localities. It usually occurs in fibrous compact masses in trachyte, of colour varying from white to red or brown, being produced by the action of sulphurous gases upon trachytic rocks rich in felspar.

The alunite from La Tolfa contains from

35 p.c. to 17·5 p.c. alumina; the average composition of the mineral is Al_2O_3 27·6 p.c., SO_3 29·74 p.c., K_2O 7·55 p.c., Fe_2O_3 1·2[illegible] p.c., SiO_2 22·7 p.c., H_2O 11·2 p.c.

Aluminium sulphate may be produced by dissolving either the hydrated oxide or the silicate in sulphuric acid. Of the raw materials available for its manufacture, the two which are of the greatest importance at the present time are china clay (kaolin) and bauxite. China clay is a very pure variety of clay, resulting from the natural decomposition of felspar, and approximating in composition to the formula $Al_2O_3,2SiO_2,2H_2O$. It is of comparatively rare occurrence, being found chiefly in Devon and Cornwall in England; at St. Yrieix near Limoges, and in the departments of Allier, Puy-de-Dome, and Brittany, in France; at Seilitz in Saxony; and at Nassau in Bavaria.

Bauxite is an impure aluminium hydroxide $Al_2O_3,2H_2O$, containing widely varying quantities of silica and ferric oxide. It is found in Ireland, in the south of France, and in Austria, Calabria, Senegal, &c. (*v.* BAUXITE).

The composition of typical commercial grades of the two minerals is given in the following table, the analyses having been made on material dried at 100°:—

Source	China clay		Bauxite	
	St.Stephen's	St. Austell	Antrim	France
Al_2O_3	40·15	41·10	41·08	64·18
Fe_2O_3	0·35	0·20	3·21	3·47
SiO_2	45·00	46·20	33·17	18·96
TiO_2	—	—		
K_2O+Na_2O	0·80	trace	—	—
H_2O (comb.)	13·70	12·50	22·54	13·39
Total	100·00	100·00	100·00	100·00

Production of aluminium sulphate from china clay.—At the present time the manufacture of aluminium sulphate from china clay is carried out on an extensive scale by a process based upon the original patent of Pochin (Pat. 1855, 14656). The clay, containing about 40 p.c. alumina, is obtained from Cornwall, and is selected as free as possible from grit and oxide of iron. It is reduced by milling and sifting to the finest possible state of division, and after a preliminary drying by exposure to a warm atmosphere, is calcined at a dull-red heat in a reverberatory furnace. The furnace is provided with three working doors, the material being introduced by the door which is most remote from the firegrate, and gradually raked forward until it reaches the hottest part of the hearth. During the calcination the clay suffers a loss in weight amounting to from 20 to 25 p.c., due to the expulsion of the whole of the moisture present (10 to 15 p.c.) and of the greater part of the water of hydration.

The calcined clay, which still contains about 3 p.c. of water, is transferred by means of iron tubs to a lead-lined wooden vat containing the requisite quantity of sulphuric acid, heated to a temperature of 85°, and having a strength at this temperature of 96° Tw. A vigorous reaction immediately takes place, and after the lapse of 15 minutes, during which period the contents of the vat are kept well agitated, the product is run into lead-lined wooden waggons (with removable sides), in which the reaction continues for a considerable time and the pasty mass gradually solidifies. Finally the solid block is brought under a heavy mechanical knife, and by a combined cutting and crushing action is reduced to the state of a coarse powder.

The product, which is brought on the market under the name of 'alum cake,' contains the whole of the silica, iron, and other impurities present in the clay, its average composition being: Al_2O_3 (soluble) 12·25 to 13·0 p.c., Fe_2O_3 0·12 to 0·22 p.c.; combined SO_3 29·5 to 31·8 p.c., free SO_3 0·4 to 1·0 p.c.; insoluble matter 20·0 to 26·5 p c.

About 60 p.c. of the alumina present in the china clay is converted into sulphate.

The commercial 'white sulphate of alumina' is prepared from alum cake in the following manner: The coarsely crushed alum cake is lixiviated with water (or with weak liquors from previous extractions) in lead-lined vats heated by live steam; after settling, the clear solution is decanted by means of a hinged pipe, and run into lead-lined evaporators, heated by steam coils, where it is concentrated to a strength of 112°Tw. at the boiling-point (about 115°). The syrupy liquid is then run into a series of shallow tiled troughs, where it solidifies on cooling. Before solidification occurs, a number of leaden partitions are inserted in the troughs, and the product is thus obtained in the form of rectangular blocks of uniform size (24″×9″×6″). 'White sulphate of alumina,' prepared by the above process, contains on an average about 14 p.c. of alumina and 0·25 p.c. of ferric oxide, and is practically free from insoluble matter. Another grade of the material is prepared containing 17·5 p.c. alumina.

Preparation of aluminium sulphate from bauxite.—The substitution of bauxite for china clay in the manufacture of aluminium sulphate was proposed by Lechatelier in 1858, and its treatment forms the subject-matter of numerous patents. Bauxite has the advantage over china clay that it is more readily soluble in acid, and needs no preliminary calcination, the chief drawback to its use being the presence of a comparatively large amount of iron.

The treatment of bauxite for the preparation of 'alumino-ferric cake,' as patented by Messrs. P. and F. M. Spence (1875), is as follows:—The mineral is digested with dilute sulphuric acid with the aid of steam until the acid is neutralised; the insoluble matter allowed to subside, and the solution evaporated to 116°Tw. and run into shallow-partitioned lead coolers. It there solidifies, and is removed in blocks 18 or 20 inches square, each weighing about 1 cwt. It is yellowish-green in colour, contains much alumina, and a small proportion of iron and free acid. It is used in the preparation of all but the finest papers, in the precipitation of sewage and refuse liquids, and in the clarification and decolourisation of water supplies. The following analysis shows its general composition: Al_2O_3 14·26 p.c. (corresponding to $Al_2O_3 3SO_3$ 47·61 p.c.), Fe_2O_3 0·28 p.c., FeO 0·32 p.c., SO_3 (combined) 35·36 p.c., SO_3 (free) 0·45 p.c. Insoluble 0·06 p.c.

The commercial sulphate of alumina which is sold under the names of 'concentrated alum' and 'alferite,' resembles alumino-ferric in composition, and is prepared by a similar process. The following details concerning its manufacture will serve to exemplify modern practice.

As raw material, it is usual to employ a mixture of Irish and French bauxites, reduced by means of disintegrators to the state of a coarse powder. The powdered mineral is conveyed by means of an elevator to a lead-lined vat containing sulphuric acid, heated to its boiling-point (about 125°), and having a strength, at this temperature, of 70°Tw. The mixture of acid and bauxite is boiled vigorously for 6 hours, after which it is diluted with weak liquors to 70°Tw. (measured at the boiling-point) and allowed to settle. The clear liquor is decanted and evaporated in lead-lined vessels until its density reaches 112°Tw. (boiling). It is then run into partitioned coolers where it solidifies, forming blocks or slabs, containing on an average 13·8 p.c. alumina, 0·7 p.c. ferric oxide, and 0·1 p.c. insoluble matter.

If French bauxite be used alone in the above process, great difficulty is experienced in the clarification of the liquor; with a mixture of Irish and French bauxites, however, rapid settling occurs, and a perfectly clear liquor is readily obtained. It is of importance also, in this connection, that the liquor should retain a small amount of free acid, as the fully neutralised solution settles very slowly.

Sulphate of alumina prepared by any of the above processes always contains appreciable quantities of iron, and the removal of this impurity is a problem of considerable importance, and one which has received the attention of many chemists. Numerous processes have been devised for the purpose, but it is doubtful if any of these is satisfactory in works' practice.

Newlands (Eng. Pat. 1880, 5287) evaporates a crude solution of the sulphate to a density of 67°Tw. (at 200°F.) and cools for twenty-four hours in leaden tanks.

About 60 p.c. of the sulphate thus crystallises out. The liquid is drained off, and the residue pumped or forced into lead-lined filter presses, the plates of which are covered with thick felt, and separated by metal rings. Here it is subjected to a pressure of about 200 lbs. to the square inch. The hard cake so produced contains about 67 p.c. of the total aluminium sulphate, and 0·05 to 0·1 p.c. of iron. The mother liquor, evaporated and similarly treated, yields a second and third crop of crystals containing increasing quantities of iron.

Chadwick and Kynaston have patented a method for the removal of iron from bauxite before converting the latter into aluminium sulphate. The powdered mineral is mixed to a thick cream with water, and treated with 5 to 10 p.c. of oxalic acid and sufficient hydrochloric acid to prevent the formation of insoluble oxalates. After seven to ten days the mass is washed, and a large proportion of the iron (together with some of the alumina) is thus removed as oxalate.

Condy, in 1877, proposed the reduction of the iron by reducing agents, or its conversion into sulphide by sulphuretted hydrogen, and the removal of the metal or sulphide by dilute acid. The proportion of iron may thus be reduced to one-third.

Weismann suggested the precipitation of the iron from aluminium sulphate liquors by means of potassium ferrocyanide. The method is by no means satisfactory, as the precipitate contains much alumina and subsides very slowly.

Kynaston precipitates the bulk of the iron as ferric arsenite, removing the last portions with calcium ferrocyanide, followed by the addition of copper or zinc sulphate.

According to Fahlberg and Semper (Eng. Pat. 1881, 5579), both ferrous and ferric salts may be precipitated from aluminium sulphate by agitation in the cold for about thirty minutes with lead peroxide, ferrous salts being first oxidised and then precipitated. No lead passes into solution unless chlorides be present. The composition of the precipitate is not known, but the peroxide may be regenerated by digestion in cold nitric acid. P. and F. M. Spence (Eng. Pat. 1882, 3835) use manganese dioxide for the same purpose. In presence of reducing agents such as ferrous salts, &c., manganese passes into solution, and requires to be reprecipitated by addition of chlorine or a hypochlorite.

The use of metantimonic acid and metastannic acid (Hood and Salamon) has also been proposed for the precipitation of iron. The iron is first oxidised by the addition of bleaching powder, and the liquid is neutralised with chalk and agitated with the precipitant. Both substances may be regenerated by digesting the precipitate with sulphuric acid.

According to H. Spence, W. B. Llewellyn, and P. Spence and Sons (Eng. Pats. 23036, 1904; 3805, 1912; 9148, 1914), the crude liquor, which must be basic and have all the iron in the ferric state, is treated with potassium sulphate and agitated for several hours at from 60° to 80° until most of the iron is precipitated as insoluble basic ferric sulphate. J. Boulton (Eng. Pat. 20227, 1914) proposes to neutralise the free acid in and remove iron and other impurities from crude aluminium sulphate by immersing in the liquor a framework of magnetised steel wire with cross wires of copper holding zinc rods in suspension. The process is carried out for six hours at 38°.

(For further information regarding these processes, *see* Beveridge, J. Soc. Chem. Ind. 1886, 16–22; B. E. R. Newlands, *ibid.* 1882, 124; Kynaston, Chem. News, 40, 191 and 202.)

Most of the above-mentioned processes for the purification of aluminium sulphate from iron possess little or no commercial significance at the present time. 'Pure aluminium sulphate' is prepared directly from *pure* alumina, which is obtained from French red bauxite by the 'alkali fusion' process. The bauxite, after a preliminary roasting, is reduced to a fine powder, and mixed with soda ash in such proportions that for every molecule of Al_2O_3 present there are 1 to 1·5 molecules of Na_2O. The mixture is strongly heated in a reverberatory furnace, with frequent stirring, for a period of five hours. Carbon dioxide is evolved and the alumina and ferric oxide are converted into sodium aluminate and sodium ferrite respectively. The mass is lixiviated by successive extractions, first with weak liquor from previous batches, and finally with pure water. The sodium aluminate dissolves as such, whilst the sodium ferrite is decomposed, forming insoluble ferric oxide which remains in the exhausted residue, and caustic soda which passes into solution. The clear liquor is run into a boiler and saturated with carbon dioxide produced by the combustion of coke or by the decomposition of limestone. During the passage of the gas the contents of the boiler are heated to 70° C. and kept thoroughly stirred by means of an agitator. When the precipitation of the alumina is complete, the liquid is allowed to settle and the clear liquor decanted and concentrated for the recovery of the dissolved sodium carbonate, whilst the alumina is drained in a hydro-extractor.

A cheaper process for obtaining the alumina from the sodium aluminate has been devised by Bayer, as already described.

The alumina prepared by either of the above processes yields by treatment with sulphuric acid, a very pure quality of aluminium sulphate. Two grades of the latter are commonly prepared for the English market—the one, sold in the form of slabs or blocks, contains 14·0 p.c. of alumina and 0·0025 p.c. of ferric oxide, the other, sold in powder, contains 17·0–18·0 p.c. of alumina and 0·0040 p.c. of ferric oxide.

Aluminium sulphate crystallises with difficulty in thin, six-sided nacreous plates, containing 18 molecules of water and having a density of 1·6913 at 17° C. (Dewar). The following table of solubilities is given by Poggiale (Ann. Chim. Phys. [3] 8, 467) for the crystalline and anhydrous salts :—

Temp. °C.	Solubility in 100 parts of water	
	$Al_2(SO_4)_3$	$Al_2(SO_4)_3,18H_2O$
0	31·3	86·8
10	33·5	95·8
20	36·1	107·3
30	40·4	127·6
40	45·7	167·6
50	52·1	201·4
60	59·1	262·6
70	66·2	348·2
80	73·1	467·3
90	80·8	678·8
100	89·1	1132·0

The addition of alcohol, in which aluminium sulphate is almost insoluble, to aqueous solutions of aluminium sulphate, facilitates the crystallisation of the salt (Persoz).

When heated, aluminium sulphate melts in its water of crystallisation, swells up, and gradually forms a white porous mass of the anhydrous sulphate, which only dissolves slowly in water. At a red heat oxides of sulphur are expelled and a residue of pure alumina remains.

Aluminium sulphate combines readily with the sulphates of the alkali metals, forming crystalline double sulphates, known as alums, which are, as a rule, considerably less soluble than aluminium sulphate itself. According to Reuss (Ber. 17, 2888), the addition of 1 p.c. of potassium sulphate to a solution containing 7 p.c. or upwards of aluminium sulphate, at once produces a crystalline precipitate of alum.

The general industrial uses of aluminium sulphate are the same as those of ordinary alum. It is largely used in paper-making, water purification, and in the preparation of red liquor as a mordant. The coarser preparations are employed for the precipitation of sewage.

Karl Reuss (Ber. 17, 2888) gives the density of solutions of pure anhydrous aluminium sulphate as follows :—

Percentage	Density at 15°C.	Percentage	Density at 15°C.
1	1·017	14	1·1467
2	1·027	15	1·1574
3	1·037	16	1·1668
4	1·047	17	1·1770
5	1·0569	18	1·1876
6	1·0670	19	1·1971
7	1·0768	20	1·2074
8	1·0870	21	1·2168
9	1·0968	22	1·2274
10	1·1071	23	1·2375
11	1.1171	24	1·2473
12	1·1270	25	1·2572
13	1·1369		

Percentage	Density at 25°C.	Density at 35°C.	Density at 45°C.
5	1·0503	1·0450	1·0356
10	1·1022	1·0960	1·0850
15	1·1522	1·1460	1·1346
20	1·2004	1·1920	1·1801
25	1·2483	1·2407	1·2295

For further particulars regarding the manufacture of aluminium sulphate, *see* The Mineral Industry, iii. 25; and Manufacture of Alum and other Salts of Alumina, by L. Geschwind, Scott, Greenwood and Co., London.

The production of aluminium sulphate, alum cake, alums and other aluminium compounds is carried out in large quantities in the United States. The total output of these products in 1912 approached 160,000 tons, and rose steadily to 296,000 tons in 1917.

For the detection of free acid in aluminium sulphate, a dilute solution of Congo red is useful, becoming blue in presence of free acid, but is not affected by the pure salt.

For the estimation of the free acid, a weighed quantity (20 to 50 grams) of the sample is dissolved in 40 to 100 c.c. of water, the solution heated to boiling, and titrated with normal caustic soda until a drop of the liquid, taken out with a glass rod, fails to yield a blue colour when mixed with six drops of Congo red solution (prepared by dissolving 0·067 gram of Congo red in 100 c.c. of boiling water and diluting to a litre). The presence of iron salts interferes with this method as ferric sulphate, for example, reacts acid towards Congo red.

T. J. I. Craig (J. Soc. Chem. Ind. 1911, 184) proposes to determine the free acid in aluminium sulphate by treating the latter with excess of neutral potassium fluoride, whereby the double salt $AlF_3 \cdot 3KF$ is formed together with potassium sulphate. As these products are neutral to phenolphthaleïn, the free acid present may be directly titrated with a standard solution of potassium hydroxide.

Iron, in the ferrous condition, is estimated by titration with decinormal potassium permanganate, and total iron by means of standard titanous chloride solution (*v.* Knecht and Hibbert, New Reduction Methods in Volumetric Analysis; and Ber. 1903, 1550). If the quantity of iron present be very small, it is determined colorimetrically (*v.* ALUMS).

Several basic aluminium sulphates have been prepared. The compound $Al_2O_3,2SO_3,12H_2O$ is obtained by heating a solution of aluminium sulphate with zinc, or by dissolving in it the calculated quantity of aluminium hydrate. Spence and Sons, Limited (D. R. P. 1903, 167419), prepared a basic sulphate of similar composition by heating sulphuric acid under pressure with 15 to 30 p.c. more alumina than is required for the formation of the normal salt. The solution is then treated with sufficient chalk or lime to raise the basicity by 20 to 28 p.c. The strongly basic solution is rapidly filtered and concentrated *in vacuô* until its density reaches 1·45. On cooling with agitation, a magma of crystals is formed and is separated by suitable means from the mother-liquor which contains normal aluminium sulphate (*cf.* also Eng. Pat. 1902, 25683, and Fr. Pat. 1903, 331836).

Aluminium sulphite $Al_2O_3(SO_2)_3$.

The bisulphite has been used by Becker (Dingl. poly. J. 257, 300), Suchomel (J. Soc. Chem. Ind. 1887, 143) and others, for the purification of beet sugars. Becker prepares for this purpose a solution of sp.gr. 1·167 containing 4·37 p.c. alumina and 13·9 p.c. sulphurous oxide, by dissolving the hydrated oxide in sulphurous acid.

Aluminium phosphates. As hydrated phosphate, aluminium occurs in the *turquoise*, and enters into the composition of *wavellite*, *lazulite* and *gibbsite*. It is found in considerable quantity in mineral phosphates, as in the Redonda phosphates which have been used for the preparation of alum and for fertilisers (*v.* ALUMS; MANURES). A massive stony variety is found on the island of Anguilla in the West Indies.

Aluminium thiocyanate or **sulphocyanate** has been proposed as a substitute for aluminium acetate for alizarin, steam reds, &c.; the colours produced are said to be especially permanent (*v.* Storch and Ströbel, Dingl. poly. J. 241, 464; and Gottlieb Stein, Dingl. poly. J. 250, 36).

Lauber and Haussmann (Dingl. poly. J. 245, 306) recommend the following method of preparation: 5 kilos aluminium sulphate are dissolved in 5 litres boiling water, 250 grams of chalk are added, followed by 11·5 litres of crude calcium thiocyanate solution of 30° Tw., and the whole well stirred and allowed to settle. The clear liquid is ready for use.

Aluminium permanganate *v.* MANGANESE.

Aluminium silicates. These compounds are exceedingly numerous and important. As an anhydrous silicate, with silicate of iron, calcium, magnesium, &c., aluminium occurs in the varieties of *garnet*, crystallising in the regular system. As silicate of aluminium, calcium, and sodium it is found in *lapis-lazuli*, which was formerly used as *ultramarine*. It is now replaced by artificial ultramarine (*v.* ULTRAMARINE). As silicate of aluminium, combined with potassium, iron, and magnesium, it occurs in the *micas*. As double silicate of aluminium, potassium, sodium, magnesium, or calcium, it forms the varieties of *felspar* which occur in immense quantities in eruptive rocks. By the decomposition of felspar by the carbonic acid in the atmosphere and in rain or spring water, the alkaline compounds are removed, leaving kaolin or clay of more or less purity (*v.* CLAY), which, under pressure, becomes hardened and laminated, forming *shale*, and finally *slate* (*q.v.*). Many of the silicates of aluminium are of great importance, and of the widest application. The more important of them are specially considered under their applications (*v.* POTTERY; PORCELAIN).

Aluminium acetate. *Red liquor* (*v. Aluminium acetates*, art. ACETIC ACID).

Aluminium ethoxide is prepared by treating anhydrous alcohol with aluminium in presence of a small quantity of mercuric chloride (as a catalyst) and iodine or alkyl haloids. The mixture is distilled under reduced pressure when a distillate free from mercury is obtained (Farbwerke vorm. Meister Lucius and Brüning, D. R. P. 286596; J. Soc. Chem. Ind. 1915, 34, 1168).

Aluminium oleate is a soft white, putty-like substance, of great tenacity, insoluble in water, soluble in ether and petroleum. A mixture of oleate, palmitate, and other fatty salts is produced from whale, cotton-seed, and similar oils by saponification with soda and addition of the sodium salt so produced to a solution of alum. The gummy precipitate is known as 'oil pulp,' and is dissolved in 4 or 5 parts of mineral oil to form a 'thickener' for addition to the lubricator. A sample of oil pulp resembling thick gelatin had a sp.gr. of 0·921, and contained 6 p.c. alumina combined with 30 p.c. fatty acids, together with 15 p.c. lard oil, and 48 p.c. paraffin oil (Oil and Colourman's Journ. 4, 403).

Aluminium palmitate is a constituent of oil pulp. It may be prepared in the same manner as the oleate, from palm oil. It forms a resinous, elastic, inodorous, neutral substance, insoluble in water, but readily soluble in petroleum and turpentine. K. Lieber (Dingl. poly. J. 246, 155) recommends the use of the latter solution as a varnish. It imparts a glossy appearance to paper, leather, &c., and renders them waterproof without affecting their elasticity.

The compounds of aluminium with the higher fatty acids are used for increasing the viscosity of mineral lubricating oils, under the names 'oil pulp' and 'fluid gelatin' (L. Marquardt, Zeitsch. anal. Chem. 25, 159). G. H. B.

ALUMINIUM BRONZE *v.* ALUMINIUM.

ALUMINIUM FOIL AND POWDER, *Manufacture of.* The following is an account of the processes conducted at La Praz and Charleville-sur-Audelle by the Société française de Couleurs métalliques, for the manufacture of aluminium foil and powder. In the manufacture of aluminium foil the metal, delivered to the works in the form of ingots, 700 × 320 × 120 mm. (cast at 750°–775° C.) is first hot-rolled at 420° C. to a thickness of 3·5 m. and then cut into strips 8 cm. wide, which, after being annealed at 420° C., are cold-rolled to 0·04 mm. in six stages, further reduction in thickness being then effected by continued rolling or by hammering. In the former case the metal bands are first greased, then rolled in pairs to 0·02 mm., and subsequently in fours to the desired thickness of 0·01 mm., the foil thus being obtained in lengths of about 16 m. In the latter case, the bands are made into packets of 500 each and beaten by pneumatic hammers, each packet being placed between two thin sheets of zinc; when the thickness of the metal reaches 0·03 mm. the packets are hammered in pairs to 0·02 mm.. and then in fours to 0·01 mm. The wastage in either case is very considerable, only about 33–35 p.c. of the 0·04 mm. metal employed being obtained as good foil, one square inch of which weighs about 27 grams; the waste foil is used for the production of aluminium powder. Before being finally trimmed and cut to size, the sheets of foil are either mechanically separated, or embossed by means of suitable rolls, since—in the absence of the layers of air thus introduced between the sheets—the metal is liable to become autogenously soldered at the cut edges. In the manufacture of aluminium powder it has been found necessary to employ the foil as the raw material, the powder yielded by other forms of the metal being of too granular a character for use in the preparation of paint. The comminution of the foil is conducted in a series of stamp mills, in each of which the closed mortar-box is provided with a circle of twelve stamps actuated from a central shaft, to the lower end of which a scraper or plough is attached. Caking of the metal is prevented by the scraper, which also causes the charge to be periodically thrown against the screen inserted in the side of the mortar; the screen is provided with an exterior sliding box for collecting the metal passing through. After further classification, the finer portion of this product is mixed with about 2 p.c. of stearine (to prevent agglomeration and autogenous soldering of the particles during the fine grinding) and passed to a second series of stamp mills, the product from which is screened through silk bolting cloth (No. 200). The powder passing through the latter is then classified by a kind of winnowing process in 'elevators,' each comprising a vertical brass cylinder, 2 m. high and 0·80 m. in diameter, in which a central vertical spindle—to which horizontal wings or paddles are attached—is adapted to rotate, and provided with receptacles arranged at different levels upon a helical rail attached to the inner wall. The powder is fed through a tube into the lower part of the cylinder, the rotation of the spindle being so adjusted that the lighter particles or flakes become suspended in the air, and are deposited in the peripheral receptacles at levels corresponding to their weight and physical condition; the coarser particles remaining at the bottom of the cylinder are returned to the fine-grinding mills. The product from the 'elevators' is finally treated for ten hours in polishing machines, consisting of horizontal, rotatory cylinders of striated steel, 1·20 m. long and 0·60 m. in diameter. The polishing of the metallic powder is effected by means of brushes attached to the axis and bearing upon the interior wall of the cylinder through the whole of its length. Since conditions favourable to ignition or explosion are liable to be developed within the fine-grinding mills, elevators and polishing machines, the various units are of relatively small capacity, and are so disposed, both in relation to each other and to the other portion of the works, as to localise any damage that may arise from this cause (Guillet, Rev. Mét. 1912, 9, 147; J. Soc. Chem. Ind. 1912, 31, 339).

ALUMNOLE. $[C_{10}H_5OH(SO_3)_2]_3Al_2$ Trade name for aluminium naphthol sulphonate. Produced by the action of aluminium sulphate on the barium salt of β-naphthol disulphonic acid R. Used as an antiseptic.

ALUMS. This generic name is given to an important group of double salts of the general type $R_2SO_4,R'_2O_3(SO_3)_3,24H_2O$, where R is a monovalent metal or basic radical such as potassium, sodium, ammonium, &c., and R'_2O_3 is a sesquioxide such as that of aluminium, iron, chromium, or manganese. They are all soluble in water, and crystallise therefrom with twenty-four molecules of water, in forms belonging to the regular system, usually octahedra or cubes.

The alums which contain the sesquioxide of alumina will alone be considered here, and of these the most important are the potassium, sodium, and ammonium compounds.

'Selenic alums' have been prepared, in which sulphuric acid is replaced by selenic acid.

Potassium alum, *Potash alum*

$$K_2SO_4,Al_2O_3(SO_3)_3,24H_2O.$$

This salt is found in nature as *kalinite*, in the form of fibrous crystals or as an efflorescence on aluminous minerals, and occasionally also in octahedra, at Whitby, Campsie, &c. In the Solfatara near Naples, and the islands of Volcano and Milo, it occurs in larger quantities, being formed by the action of volcanic gases upon felspathic trachyte.

Of greater importance is the mineral *alunite* or *alumstone*, which is a double salt of potassium sulphate and basic aluminium sulphate, having the composition $K_2SO_4,Al_2(SO_4)_3,2Al_2(OH)_6$; it is found at La Tolfa near Civita Vecchia; at Montioni in the Duchy of Piombino; at Mursaly, Munkact, and Tokay in Hungary; in the islands of Milo, Argentino, and Nipoglio (Grecian Archipelago); at Puy-de-Sancy and Madriat (Auvergne); at Samsoun in Asia Minor; and in Australia. An 'alum mountain,' composed of this mineral, is reported to exist in China, and is stated to be nearly 1900 feet high and to have a circumference at its base of about ten miles (U. S. Cons. Report, 1903).

The manufacture of alum is of great antiquity. In the time of Pliny alum was in use as a mordant for the production of bright colours, and was even tested by means of the *tannin* in pomegranate juice to ascertain its purity. It was prepared in the thirteenth century at Smyrna from alum rock, and since the fifteenth century has been largely produced at La Tolfa from the same substance.

Its preparation from pyritic shale has long been known, together with the fact that the presence of an alkali was necessary to induce crystallisation, but, until proved in 1797 by Chaptal and Vauquelin, the essential presence of alkali in the crystals was not recognised.

Very pure alum is prepared in small quantities at Solfatara. The natural alum found there is digested with water in large wooden vats under cover, and maintained at about 40° by the natural heat of the soil. The solution is decanted and crystallised. A second crystallisation produces extremely pure alum.

Production of alum from alunite.—The preparation of alum from alunite is an industry which dates from very early times. Of Oriental origin, it appears to have been introduced into Europe in the thirteenth century, and during the fifteenth century several alum works were established. Amongst these may be mentioned the celebrated works at La Tolfa near Civita Vecchia, a district in which alum manufacture still ranks as an important industry.

The outline of the La Tolfa process given below is of historical interest. The mineral, broken into lumps of moderate size, is calcined at a low red heat, either in heaps or in kilns. The operation requires to be carefully performed, and is stopped as soon as the mineral begins to evolve acid fumes. The calcination occupies about six hours and results in a loss in weight amounting to about 33 p.c., chiefly due to the expulsion of water; at the same time the basic sulphate is decomposed, yielding alum and insoluble alumina. The roasted mass is transferred to brickwork bins and exposed to the air for several months, during which time it is occasionally moistened. The resulting sludge is lixiviated with water at 70°, and the clear decanted liquor concentrated. The crystals of alum which separate on cooling are cubic and have a reddish tinge owing to the presence of suspended ferric oxide; this may be removed by recrystallisation. The amount of soluble iron present is stated to be less than 0·005 p.c. The product, known as Roman alum, was in former times highly valued on account of its great purity.

In the modern process, employed on the Continent, the alunite is calcined at a higher temperature and the product treated with sulphuric acid, whereby aluminium sulphate is formed from the excess of alumina, and passes into solution together with the alum. The latter is either crystallised out, and the more soluble aluminium sulphate recovered as such from the mother liquors, or sufficient potassium sulphate is added to convert the whole of the aluminium sulphate into alum.

According to C. Schwartz (Ber. 17, 2887), the best temperature for the roasting is 500°, and the acid used should have a density between 1·297 and 1·530. L. Geschwind (Manufacture of Alum and the Sulphates of Alumina and Iron, 1901), however, states that in France a temperature of about 1000° is employed.

Formerly, the greater portion of the alum manufactured in England was prepared from alum shale (alum ore), alum schist, and similar minerals, which occur in large quantities at Whitby in Yorkshire, Hurlet and Campsie in Scotland, in Sweden, Norway, Belgium, and in several parts of Thuringia, Westphalia, &c. These minerals are mixtures of aluminium silicate, iron pyrites, and bituminous substances; the iron pyrites is principally present in the aluminous schists as a fine black powder, disseminated throughout the mass, and not distinguishable to the eye. The rapid oxidation of these minerals under atmospheric influences or heat is due to this state of fine division.

Aluminous earths are dark brown, friable, porous masses without structure, and contain less silica than the schists. They usually occur in layers with lignite.

Production of alum from aluminous shale.—The more earthy shales are porous, and if piled in heaps in the open air and occasionally moistened undergo spontaneous oxidation, with the formation of sulphates of iron and aluminium. Usually they require roasting, and when not sufficiently bituminous for combustion, are first mixed with fuel.

The coarsely broken shale is built up with alternate layers of coal into heaps, which are ignited. As the mass burns, fresh quantities of the mineral are added, until a sufficient mass of material has been accumulated. By pumping water over the surface at intervals the temperature is regulated to a degree suitable for rendering the decomposition as complete as possible. Too high a temperature is to be avoided, as it results in the loss of sulphur dioxide and the formation of a slag. During the combustion of the shale the pyrites is decomposed, giving up a portion of its sulphur, which is converted by burning into sulphur dioxide, and this in conjunction with atmospheric oxygen attacks the clay, forming aluminium sulphate. The calcined mass is allowed to remain exposed to the air for a considerable period, during which a further absorption of oxygen takes place, resulting in the conversion of the lower sulphide of iron into ferrous sulphate and ferric oxide.

Lixiviation.—This operation is carried out in large lead-lined boxes with perforated bottoms, the filtering bed being formed of timber topped with brushwood. A layer of the roasted mineral about 13 inches deep, is introduced and its extraction is effected, first with the mother liquor from the alum crystallising pans, and later with pure water, the liquid in each case being left overnight in contact with the material.

The exhausted mineral still contains a considerable amount of alumina and sulphuric acid. The liquors, which have a density of 1·09 to 1·15, are run into settling tanks and allowed to deposit calcium sulphate, ferric oxide, and other suspended impurities, and are then removed for concentration. The method adopted for this purpose varies according to the nature of the mineral under treatment. In the case of shales from Hurlet and Campsie the concentration is effected by surface evaporation in a reverberatory furnace.

The bed is of stone, coated with well-rammed clay, 4 or 6 feet wide, 2 or 3 feet deep, 30 or 40 feet long. It is filled to the brim with strong liquor, and the flame and hot air from the fire carried over it. As evaporation proceeds, more liquor is added until the proper concentration is reached. It is then run into leaden pans, concentrated to about 1·4 sp.gr. and conveyed to a precipitating cistern containing the requisite quantity of dry potassium chloride; the liquid is well agitated and the chloride soon dissolves.

In about 5 days the liquor is drained from the large crystals, which are washed and recrystallised.

The Whitby shales differ from those at Hurlet, in that they contain a considerable quantity of magnesia which passes into the extract in the form of magnesium sulphate. In this case surface evaporation is not satisfactory on account of the formation of a crust of this salt which retards evaporation. The evaporation of the liquor is carried out, therefore, in leaden vessels, until a sp.gr. of 1·125 to 1·137 is reached, after which the solution is allowed to stand until clear. The concentration is continued up to sp.gr. 1·25, at which stage a sample of the liquor is withdrawn and the percentage content of aluminium sulphate determined. After further evaporation to a density of 1·4 to 1·5, the hot liquor is run into a precipitating tank and mixed with a saturated solution of the calculated quantity of potassium chloride or sulphate, the whole being kept in constant agitation to induce the formation of small crystals (alum meal).

When much ferric sulphate is present in the solution, the addition of potassium sulphate would produce iron alum, isomorphous with ordinary alum, which would crystallise out and contaminate the product. The use of potassium chloride prevents this, by producing the easily soluble ferric chloride, while ferrous salts are converted into the equally soluble ferrous chloride, an equivalent amount of potassium sulphate being formed at the same time. Chloride of potassium is generally employed in preference to the sulphate, whenever sufficient iron sulphate is present to supply the requisite amount of sulphuric acid for the formation of alum; its greater solubility is also in its favour. Too much chloride should be carefully avoided, for after the iron sulphates have been decomposed, the aluminium sulphate is itself attacked, with the production of the very soluble chloride, which is lost.

The *alum meal*, consisting of small brownish crystals, is drained and washed twice with cold water. The adhering mother liquor, containing much iron, is thus removed, and the meal is left nearly pure. The final purification is effected by dissolving in a minimum quantity of boiling water and allowing the solution to stand for about eight days in casks furnished with movable staves. At the end of this period the staves are removed, and after two or three weeks further standing, the block of crystals is pierced, the mother liquor drained off and employed for dissolving fresh quantities of meal.

The mother liquor from the alum meal has a sp.gr. of about 1·4; it contains sulphate or chloride of iron, magnesium sulphate, &c., and will yield more alum on evaporation. In a final evaporation it yields ferrous sulphate in fine green crystals. When iron is present in large quantity, the liquors are evaporated and the ferrous sulphate crystallised out before the addition of the potassium salt. In this case the iron salt is less pure and less soluble, but the alum subsequently produced contains less iron.

Formerly, potassium alum was alone produced. In 1845, however, the potassium sulphate was replaced by the ammonium sulphate produced from the then waste liquors from gas works, yielding ammonium alum. This great improvement was introduced by the late Peter Spence; his method was soon generally adopted both in England and on the Continent.

Another great advance was made by Spence in 1845 in the manufacture, by the treatment of the refuse shale underlying the coal-seams of South Lancashire. This shale contains from 5 to 10 p.c. of carbonaceous matter. It is piled upon rows of loosely placed bricks (to allow a free passage to the air) in heaps 4 or 5 feet high and 20 feet long. The combustion is started with a little fuel, but the shale contains sufficient combustible matter to continue burning. The calcination is performed slowly at a heat below redness. In about 10 days the roasting is completed, and the material has become soft, porous, and light-red, whilst the alumina contained in it has become anhydrous and soluble in sulphuric acid. Too high a temperature, however, partially vitrifies it, in which case it is only slowly attacked by acid. Charges of 20 tons are placed in large covered pans 40 feet long, 10 feet wide, and 3 feet deep, lined with lead, and are digested for about 48 hours with sulphuric acid (of sp.gr. 1·35) at 110°, the temperature being maintained by fires beneath the boilers. Formerly ammonia was forced into the liquid from a boiler containing gas liquor; ammonium sulphate was thus produced, with considerable rise of temperature, and combined with the aluminium sulphate forming ammonium alum. The solution of alum so produced is run into cisterns 29 feet by 17 feet, and 1½ feet deep, in which it is kept in constant agitation. In about 14 hours the small crystals so formed are drained, washed with some mother liquor from 'block alum,' and dissolved by a process known as 'rocking' for the production of pure block alum. For this purpose they are introduced into a hopper, at the bottom of which they encounter a current of steam at a pressure of 20 lbs. per sq. inch, both steam and crystals being supplied in such proportions that all the crystals are dissolved, while no steam is wasted. In this manner 4 tons of crystals may be dissolved in 30 or 40 minutes. The solution is run into a leaden tank, and, after a time, treated with a small quantity of size, which precipitates a quantity of insoluble matter. The clear liquid is next run into tubs about 6 feet high and 6 feet wide, tapering upwards, with movable lead-lined staves. After some days the staves are removed and a hole is bored in the mass of crystals for the removal of the liquor. Each block weighs about 3 tons, while the mother liquor contains about 1 ton.

To produce 1 ton of ammonium alum by this method on an average about 15 cwts. of the shale is required.

A great advantage of this process is the speed with which the crude material is converted into marketable alum. By the old process twelve months was required for this conversion, whilst by Spence's process the whole operation is performed in one month. For this process Spence was awarded the medal for alum manufacture at the Exhibition of 1862, at which date he manufactured 150 tons of alum weekly, over one-half the total production of England (*v.* Hofmann's Report on Chemical Processes at the Exhibition of 1862, p. 62, and J. Carter Bell, Chem. News, 12, 2[illegible]

Alum is also produced by the addition of potassium sulphate to aluminium sulphate, prepared by any of the processes already described. It is prepared in great purity from the sulphate produced from cryolite; 1 ton of cryolite produces 3 tons of alum (*v. Sodium aluminate*).

Many other processes have been proposed and used for the preparation of alum.

Spence, in 1870 (Eng. Pat. 1676), patented a method of preparing alum from mineral phosphates, especially that from Redonda near Antigua, which contains 26·1 p.c. of alumina as phosphate with ferric oxide and silica. It is calcined at a red heat to render it porous, powdered, and digested with sulphuric acid of sp.gr. 1·6 in quantity proportional to the amount of alumina, in lead-lined vessels, heated by steam. The liquid is concentrated to a density of 1·45, and treated with the requisite amount of potassium sulphate to convert the whole of the alumina into alum. Phosphate containing 20 p.c. of alumina yields about 1½ times its weight of alum, from which, however, the last traces of phosphoric acid are removed with difficulty. The phosphoric acid in the mother liquors is valuable as a manure.

Methods have frequently been proposed for the preparation of alum from felspar. Ordinary felspar contains both potassium and aluminium combined with silica in larger proportions than are contained in alum; the problem to be solved is the substitution of sulphuric acid for silica. A method adopted by Turner, said to have been originated by Sprengel, consisted in the ignition of a mixture of one part of the powdered mineral with one part of potassium bisulphate until fused; one part of sodium carbonate was then added, and the whole again fused. The mass was boiled with water and the insoluble double silicate remaining was decomposed by hot sulphuric acid of sp.gr. 1·20, and the alum crystallised out. On account of the high temperature required, this process was not successful.

At the present time the bulk of the alum manufactured in England is prepared either from shale or alunite or from the aluminium sulphate derived from bauxite or china clay.

For the more delicate dyes the alum used must be of extreme purity. Samples containing even less than 0·001 p.c. of iron may be unsuitable for certain purposes. The percentage of iron in alum or in aluminium sulphate is usually determined by means of a solution of ammonium thiocyanate standardised with iron alum. Many precautions are necessary in performing the analysis (*v.* Tatlock, J. Soc. Chem. Ind. 1887, 276; G. Lunge, Mon. Sci. 1897, 160).

Potash alum crystallises with 24 molecules of water, in crystals belonging to the cubic system, usually in large colourless octahedra of sp.gr. 1·751 (Retgers, Zeitsch. physikal. Chem. 3, 289; J. B. 1889, 148).

De Boisbaudran has also obtained it crystallised with hemihedral faces of the tetrahedron. The crystalline form is affected by the presence of other substances in solution, and by the temperature. When formed at ordinary temperatures in the presence of basic alum, the crystals are cubes, frequently dull on the surface from the presence of the basic salt; for this reason Roman alum usually forms cubes. At 40° C., even in presence of basic salts, octahedra are produced.

Potash alum possesses the property of crystallising with hydrogen peroxide (Willstatter, Ber. 36, [1903] 1828).

According to Poggiale (Ann. Chim. Phys. [3] 8, 467), the solubility of potash alum and of ammonia alum is as follows:—

100 parts water dissolve:

°C.	Crystallised Potash alum.	Crystallised Ammonia alum.
0	3·9	5·2
10	9·5	9·1
20	15·1	13·6
30	22·0	19·3
40	30·9	27·3
50	44·1	36·5
60	66·6	51·3
70	90·7	72·0
80	134·5	103·0
90	209·3	187·8
100	357·5	421·9

Conductivity determinations, made on alum solutions of different concentrations, indicate that even at moderate dilutions the alum is resolved into its component salts.

Potash alum possesses a sweetish astringent taste and a strongly acid reaction. The aqueous solution decomposes when heated with precipitation of a basic alum, especially when dilute. For this reason a small quantity, not sufficient to be distinguished by taste, is frequently added to impure water. The gelatinous precipitate carries with it the colouring matter and most of the organic impurities, producing a slimy deposit.

Alum is almost insoluble in a saturated solution of aluminium sulphate, and is quite insoluble in alcohol. On exposure to air, the crystals become white on the surface. This change is due, not to the loss of water, but to the absorption of ammonia from the air, with formation of a basic salt. Below 30° C. they lose no water; at 42° C. they evolve 11 molecules (Juttke, Chem. Zentr. 18, 777). In a closed vessel over sulphuric acid they lose 18 molecules at 61° C. (Graham) and become slowly anhydrous at 100° C., more rapidly in a current of air. Alum melts in its water of crystallisation at 92·5° C., and when heated to dull redness is converted into a porous friable mass, slowly soluble in water, known as 'burnt alum.' At a white heat alumina and potassium sulphate alone remain.

When burnt alum is mixed with one-third its weight of carbon and heated to redness, the residue is spontaneously inflammable on account of the presence of finely divided potassium sulphide, and is known as Homberg's pyrophorus. By fusing alumina with potassium bisulphate and digesting the mass in warm water, anhydrous potassium alum may be obtained in crystals of which 5 parts are soluble in 100 of water at 10° C. and 74·5 parts at 100° C. (Salm-Horstmar, J. pr. Chem. 52, 319).

On the addition of caustic soda or sodium carbonate to a solution of alum until the precipitate at first produced is only just redissolved on agitation, *i.e.* when two-thirds of the acid has been neutralised, the solution contains a neutral basic alum, known as *neutral alum*, together with sodium sulphate. This solution, on account of the ease with which it gives up its excess of alumina to the fabric, is used by dyers as a mordant. Commercial potash alum is frequently mixed with ammonia alum.

Alum is extensively used as a mordant in the dyeing industries, and in the production of other aluminium mordants such as the acetate, sulphoacetate, &c., employed in dyeing and printing and for shower-proofing fabrics. The alum used for dyeing with alizarin red must be free from iron, otherwise dull shades are produced. It is also employed in the manufacture of lake pigments, in the dressing of skins ('tawing') to produce white leather, in sizing paper, and in the production of fireproofing materials. In most of its applications, however, it is being replaced by aluminium sulphate, the use of which is considerably more economical.

Sodium alum, *Soda alum*

$$Na_2SO_4,Al_2O_3(SO_3)_3,24H_2O$$

occurs as *mendozite* in S. America and in Japan (Divers, Chem. News, 44, 218).

This alum was prepared by Zellner in 1816, by the spontaneous evaporation of a solution containing sodium and aluminium sulphates. Its existence, disputed by Ostwald, has been established by Wadmore (Chem. Soc. Proc. 21, 150; C.-B. 1905, 11, 18), who from a solution of the mixed sulphates obtained octahedral crystals having the above composition. From a hot concentrated solution it is deposited on cooling as a pasty mass which slowly becomes crystalline. Contrary to the statement frequently made, the crystals do not appreciably effloresce in the air.

Technically, soda alum may be prepared in the following manner:—To a solution of aluminium sulphate containing 675 grams of the crystalline salt per litre, and maintained at a temperature of 50° C. to 60° C., is added a solution of sodium sulphate containing 146 grams of the anhydrous salt per litre, until the liquid attains a density of 1·35; crystals of soda alum separate on cooling. The crystallisation should be effected at a temperature between 10° C. and 25° C.; at 28° C. the formation of crystals proceeds very slowly, whilst below 10° C. separation of sodium sulphate occurs (Augé, D. R. P. 1899, 50323; J. 1890, 2635).

Messrs. F. M., D. D., and H. Spence (Eng. Pat. 1900, 5644) prepare a solution of sodium sulphate saturated at 40° C. to 50° C., which is allowed to cool during agitation until a considerable proportion of decahydrated crystals have separated. The mixture of liquid and crystals is then run into a solution of aluminium sulphate containing the solid salt in suspension. There is thus obtained a large crop of well-defined soda alum crystals. Alternatively, the solid aluminium sulphate may be added to a suitable solution of sodium sulphate or chloride, in which either salt may be suspended in the solid state.

Soda alum is much more soluble at ordinary temperatures than potassium or ammonium alum, in consequence of which it is more difficult to purify from iron. On account of the lower cost of sodium salts, it would be largely used in place of other and more expensive alums, if it could be easily purified by crystallisation (*see* Eng. Pat. 1881, 5650).

Soda alum crystallises with 24 molecules of water in regular octahedra, having a sp.gr. of 1·667 (Soret). At 10·6° C. 100 parts of water dissolve 107·11 parts of the alum (Wadmore); according to Ure, the solution saturated at 15·5° C. contains 110 parts of the alum in 100 of water, and has a density of 1·296. Soda alum is insoluble in alcohol.

Ammonium alum, *Ammonia alum*

$$(NH_4)_2SO_4,Al_2O_3(SO_3)_3,24H_2O$$

occurs as *Tschermigite* in Bohemia, and in the crater of Mount Etna.

Its preparation is analogous to that of potash alum, a solution of aluminium sulphate, prepared by any of the methods already described, being treated with the equivalent quantity of ammonium sulphate, and the alum separated and purified by crystallisation.

Ammonia alum crystallises with 24 molecules of water in regular octahedra, having a conchoidal fracture and a density of 1·631 (Soret). At ordinary temperatures it is less soluble in water than potassium alum (*v.* Table of solubilities, under Potassium alum). The saturated solution boils at 110·6° C., and contains 207·7 parts of the alum to 100 parts of water (Mulder). When heated the crystals swell up and form a porous mass, losing water and sulphuric acid; at a high temperature alumina alone remains. This serves as a useful method for the production of very pure alumina.

In its general properties and uses, ammonia alum closely resembles the corresponding potassium compound. G. H. B.

ALUMNOL *v.* SYNTHETIC DRUGS.

ALUM-SHALE. A kind of shale or slate containing disseminated iron-pyrites, which, on prolonged exposure to the weather, gives aluminium sulphate, owing to the action of sulphuric acid (from the decomposition of the iron-pyrites) on the clayey material. The heaps of weathered shale are leached with water, and to the solution of aluminium sulphate and sulphuric acid so obtained potashes are added. The alum obtained by the evaporation of this solution is purified by recrystallisation. The alum-shales of Liassic age on the coast of Yorkshire, in the neighbourhood of Whitby, have been largely worked by this method since the time of Queen Elizabeth, but now the industry has become extinct. At Alum Bay in the Isle of Wight clays of Tertiary age were formerly used in the manufacture of alum, as early as 1579; and in the early part of the eighteenth century the Kimmeridge clay in Kimmeridge Bay, Dorsetshire, was also so used. Pyritous shales of Carboniferous age were formerly worked at Hurlet in Renfrewshire, large works for the extraction of alum having been erected here about the year 1800. Alum-shales in the coal-measures of the West Riding of Yorkshire are, however, still worked to a small extent near Rotherham, Barnsley, and Darton. Here the iron-pyrites is more efficiently and quickly oxidised by roasting the shale, which is afterwards steeped in shallow pits, and the concentrated liquor treated with potassium chloride.

Reference.—Special Reports on the Mineral

Resources of Great Britain, vol. v. Mem. Geol. Survey, London, 1916. *V. Alums*, art. ALUMINIUM. L. J. S.

ALUNDUM. A form of fused alumina manufactured as a refractory material and abrasive. As used in the preparation of refractory articles it is a white crystalline product containing less than 1 p.c. of impurities (oxides of iron, titanium, and silicon); it melts at 2050°-2100°, and its coefficient of linear expansion is 0·0000078. A less pure form containing 6-8 p.c. of impurities and of a reddish-brown colour is also employed; it melts at about 50° lower than the white variety, and its coefficient of expansion is 0·0000085. Alundum does not soften when within 100° of its melting-point; sp.gr. 3·93-4·0; hardness 9-10 (Moh's scale). Thermal conductivity 3-4 times that of most fire-clays. Not attacked by aqueous acids and alkalis, and only very slightly by fused alkali carbonates. Dissolved with difficulty by fused slags both acid and basic, more readily by the former. For the preparation of shaped articles it is mixed with a refractory binding agent, moulded, and fired in a ceramic kiln; the articles are usually more refractory than amorphous alumina. When treated with sulphuric or hydrochloric acid they lose up to 0·03 p.c. of their weight but are then quite unaffected. The articles are porous, and cannot be used where gas-tight vessels are required, or as protecting tubes for pyrometers. The melting-point of the bonded articles is never below 1950°, and they possess great strength, both tensile and compressive; electrical resistance 476×10^6 ohms. at 535°, 49×10^6 at 721°, 24×10^6 at 908°, and $7·5 \times 10^6$ at 1040°. Alundum muffles last 4-5 times as long as clay muffles, and are more refractory and have a higher tensile strength than quartz. Crucibles of alundum can be used for melting metals, even platinum. On account of their porosity they cannot be used for melting slags or salts, but this quality makes them specially suitable as a substitute for Gooch crucibles; no asbestos filler-layer is required, and the porosity can be so controlled that the finest precipitates may be collected in them. Alundum extraction thimbles can be cleaned by simple ignition. An alundum cement is made for lining crucibles and furnaces; it does not melt or combine with carbon below 1950°. Alundum bricks have been used in place of silica for the roofs of electric furnaces (Saunders, Amer. Electrochem. Soc. 1911; Met. and Chem. Eng. 1911, 9, 258; J. Soc. Chem. Ind. 1911, 30, 686).

ALUNITE or **ALUM-STONE.** Hydrated basic sulphate of aluminium and potassium $KAl_3(SO_4)_2(OH)_6$, containing theoretically 11·4 p.c. of potash. The potash may, however, be replaced isomorphously by soda with a passage from 'kalioalunite' to 'natroalunite' (Analysis, VI). Further, the material is often impure owing to admixture with silica and clayey matter. The mineral is usually found as white, grey, or pinkish, compact and granular masses, somewhat resembling chalk, limestone, or marble in appearance. Sp.gr. 2·58-2·75. Occasionally, minute glistening crystals, which belong to the rhombohedral system, are found in cavities in the massive material. The following analyses are of material from I and II Bullahdelah, New South Wales (I pale pink, and II chalky white, containing more silica); III and IV, Marysvale, Utah (III of selected clear pink, translucent, coarsely granular material, and IV of compact, fine-grained, porcelain-like material); V, 'calafatite' from Benahadaux, Almeria, Spain; VI, white, chalky 'natroalunite' from Funeral Range, Death Valley, California.

	I.	II.	III.	IV.	V.	VI.
Al_2O_3	37·52	37·37	37·18	34·40	37·98	38·46
Fe_2O_3	0·26	0·27	trace	trace	—	—
K_2O	9·51	5·68	10·46	9·71	9·64	1·04
Na_2O	1·12	1·08	0·33	0·56	—	6·83
SO_3	36·76	22·09	38·34	36·54	34·77	25·03
SiO_2	1·92	19·34	0·22	5·28	—	10·27
P_2O_5	trace	trace	0·58	0·50	—	—
H_2O	13·19	13·86	12·90	13·08	17·61	17·60
Moisture	0·06	0·46	0·09	0·11	—	—
	100·34	100·15	100·10	100·18	100·00	98·23

The mineral mostly occurs in connection with volcanic rocks, having been formed by the action of solfataric vapours on such rocks. In some cases, however, it may have been formed by the action of decomposing iron-pyrites on clay. Extensive deposits have long been known at Tolfa near Rome, Montioni in Tuscany, and Musaz and Bereghszasz in Hungary. An important deposit, forming wide veins in volcanic rock (andesite or dacite), has been discovered and mined near Marysvale in Utah. A detailed description of this, together with a *résumé* of the published descriptions of other deposits of commercial importance, has been given by B. S. Butler and H. S. Gale (Bull. U.S. Geol. Survey, 1912, No. 511, pp. 1-64). Other localities are in Colorado, Nevada, California, and Arizona; Kyuquot Sound, Vancouver Island, British Columbia; Bullahdelah, 60 miles north of Newcastle, New South Wales; Carrickalinga Head, on St. Vincent Gulf, 40 miles south of Adelaide, South Australia; Warnertown, near Port Pirie, South Australia; and near Sunbury, Victoria. (On the Australian deposits, *see* E. F. Pittman, The Mineral Resources of New South Wales, Dept. of Mines, N.S.W., 1901. The Alunite Deposits of Australia and their Utilisation, Advisory Council of Science and Industry, Commonwealth of Australia, Bull. No. 3, Melbourne, 1917.) Extensive deposits have also been found near Benahadaux, 10 km. from the port of Almeria in Spain (S. Calderón, Los minerales de España, 1910, ii. p. 205).

Since the fifteenth century this mineral has been exploited at Tolfa near Rome, for the manufacture of potash-alum; and the harder and more compact varieties from Hungary have been used for millstones. Now, however, the mineral is of considerable importance as a source of potash. When ignited, it gives off all its water and three-quarters of its sulphuric acid, there remaining alumina and potassium sulphate, 92 p.c. of the whole of the latter being capable of extraction in solution by this method. When roasted at a lower temperature, aluminium and potassium sulphates can be extracted by lixiviation and crystallised as potash-alum. Details of the methods of treating the mineral as practised in Australia and Utah are given in the Bulletins quoted above. The mineral may be used directly as an artificial manure; but, since the potash is not present in a soluble form, better results are obtained by first roasting.

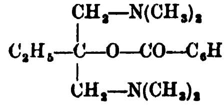
L. J. S.

ALUNOGEN. Hydrated aluminium sulphate $Al_2(SO_4)_3,18H_2O$, occurring as a white, delicately fibrous efflorescence on shale and other rocks. It has been formed by the action on the aluminous rock of the products of decomposition of iron-pyrites. A trace of iron sulphate is often present, imparting a yellowish or reddish colour to the mineral. L. J. S.

ALVA or **ALFA** *v.* ESPARTO.

ALVELOS. A name applied to the *Euphorbia heterodoxa* (Muell.), growing in Brazil, the juice of which has been used as a cure for cancer (Pharm. J. [3] 15, 614).

ALYPINE. Trade name for *benzoyltetramethyldiaminoethyldimethylcarbinol hydrochloride.*



$$\begin{array}{c} CH_2\text{—}N(CH_3)_2 \\ | \\ C_2H_5\text{—}C\text{—}O\text{—}CO\text{—}C_6H_5 \\ | \\ CH_2\text{—}N(CH_3)_2 \end{array}$$

Employed in place of cocaine and stovaine as an anæsthetic and as a remedy for vomiting and in the treatment of diseases of the upper respiratory passages and of the organ of hearing. Used also in veterinary practice in place of cocaine.

It occurs in crystals, m.p. 169°, sol. in water, forming a neutral solution. Aqueous solutions may be sterilised without undergoing decomposition by boiling from 5 to 10 minutes (Neustatter, Pharm. J. 1905, 869).

(For distinctive reactions, *v.* Lemaire, Rep. Pharm. 1906, 18, 385.) (*v.* SYNTHETIC DRUGS.)

AMADOU or **GERMAN TINDER.** (*Amadou*, Fr.; *Zunderschwamm*, Ger.). A spongy combustible substance, prepared from a species of fungus, *Fomes* (*Polyporus*) *igniarius*, the 'false' tinder-fungus, which grows on the trunks of the oak, but also on alder, willow, and various other trees. It must be plucked in the months of August and September. It may also be prepared from *Fomes* (*Polyporus*) *fomentarius*, the true tinder-fungus, also indigenous, found especially on the beech, elm, and various fruit trees. It was formerly used in surgery, and has hence been called surgeons' agaric. Amadou is prepared by removing the outer rind and carefully separating the yellow-brown spongy substance which lies within it. This substance is cut into thin slices, and beaten with a mallet to soften it, till it can be easily pulled asunder between the fingers. In this state it is useful in surgery. To convert it into tinder, it is boiled in a strong solution of nitre, dried, beaten anew, and put a second time into the solution. Sometimes, to render it very inflammable, it is imbued with gunpowder, whence the distinction of 'black' and 'brown' amadou.

AMALGAM. An alloy of mercury with some other metal or metals.

There are four general methods for preparing amalgams.

1. Metallic mercury is brought into contact with the other metal, either in the solid or in a finely divided state at the ordinary or at a higher temperature. In this way amalgams of antimony, arsenic, bismuth, cadmium, magnesium, potassium, silver, sodium, tellurium, thorium, tin, zinc, and lead may be obtained.

2. Mercury is brought into contact with a saturated solution of a salt of the metal, when part of the mercury goes into solution and the remainder combines with the liberated metal; or better still, zinc or sodium amalgam is employed, when the zinc or sodium displaces the metal in the solution. By this method amalgams of bismuth, calcium, chromium, iridium, iron, magnesium, manganese, osmium, palladium, and strontium may be prepared by using sodium amalgam, and cobalt and nickel by using zinc amalgam (Moissan, Compt. rend. 1879; Chem. News, 39, 84).

3. The metal to be amalgamated is placed in a solution of a mercury salt; copper may be amalgamated by this process.

4. The metal is placed in contact with mercury and dilute acid; this is the method usually employed in amalgamating zinc. Iron, aluminium, palladium, nickel, and cobalt may be made to combine with mercury by this process if they be placed in contact with a stick of zinc (Casamajor, Chem. News, 34, 36; Arch. Pharm. [3] 11, 64; Chem. Soc. Trans. [2] 34, 474).

Amalgams are also formed when mercury is used as the cathode in the electrolysis of salt solutions; a number of metals can thus be obtained as amalgams, although they cannot be obtained directly in the free state by the electrolysis of aqueous solutions.

The combination of sodium with mercury by method 1 takes place with great energy, heat and light being produced. The preparation is best carried out by combining a small portion of the mercury with the sodium, and then adding the remainder to the amalgam.

Native amalgams are found in various parts of the world. The table on next page contains the analyses of a few.

Gold and silver in the metallic state can be extracted from their ores by grinding the ores and making them pass through mercury, although this process is now largely replaced by the modern cyaniding methods. (For details, *v.* these metals; and May, J. Soc. Chem. Ind. 4, 352; Moon, *id.* 4, 678; Miller, *id.* 4, 122; Whitehead, *id.* 4, 503; Fisher and Waber, *id.* 4, 351; Barker, Dingl. poly. J. 251, 32; Body, *id.* 252, 33; Molloy, *id.* 254, 210; Bonnet, *id.* 254, 297; Cassel, *id.* 257, 286; Jordan, *id.* 258, 163; Hollick, *id.* 258, 168.) When the mercury has taken up a quantity of gold, the amalgam is squeezed through chamois leather, when the greater portion of the gold is left, combined with a little mercury, as a pasty mass. Kazantseff (Bull. Soc. chim. [2] 30, 20; Chem. Soc. Trans. [2] 34, 937) finds that the mercury which escapes contains at ordinary temperatures 0·126 p.c. of gold, at 0° 0·110 p.c., and at 100° 0·650 p.c., thus behaving like an aqueous solution.

Berthelot found that the solution of definite amalgams in different quantities of mercury, like the solution of salts in water, absorbs a constant amount of heat; thus the heat of solution of an amalgam of which the composition corresponds with the formula $Hg_{24}K$ in four times its weight of mercury is —8·0 kil. deg. of heat, and in twenty times —9·0 kil. deg. (Compt. rend. 89, 465; Chem. Soc. Abstr. 38, 1).

Ag	Hg	Au	Fe_2O_3	CaO	AgCl	Fe	Zn	Pb	$CaCO_3$	Cu	Insol. and loss	Locality	Analyst and reference
75·900	23·065	—	—	—	—	—	—	—	—	—	0·490	Kongsberg, Norway.	Flight. Phil Mag. [5] 9, 146.
92·454	7·195	—	0·033	0·055	0·088	—	—	—	—	—	1·328	,,	,,
36·0	64·0	—	—	—	—	—	—	—	—	—	—	Moschellandsberg Palatinate.	Klaproth, Ure 1.
25·0	73·3	—	—	—	—	—	—	—	—	—	—	,,	Heyer, *id.*
27·5	72·5	—	—	—	—	—	—	—	—	—	—	Allemont, Dauphiné.	Cordier, *ib.*
46·30	51·12	—	—	—	—	0·18	tr.	tr.	0·21	—	1·01	Salagrube, Sweden.	Nordsbröm, J. 35, 1, 521.
56·70	43·27	—	—	—	—	—	—	—	—	tr.	—	Friedrichssegen — Mine.	Weiss, J 36, 1828; Z. geol. Ges. 34, 817.
—	60·98 to 58·37	39·02 to 41·33	—	—	—	—	—	—	—	—	—	Mariposa, California	Ure.
5·00	57·40	38·39	—	—	—	—	—	—	—	—	—	Choco, New Grenada.	Schneider. Ure.

According to Berthelot, the maximum heats of formation for amalgams of potassium and sodium are 34·2 and 21·1, corresponding with crystalline amalgams containing 1·6 p.c. of potassium, and 2 p.c. of sodium respectively. In these amalgams the relative affinities of the free alkali metals are inverted: this explains Kraut's and Popp's observation that sodium displaces potassium when potassium hydroxide is treated with sodium amalgam, the final result being the formation of an amalgam of composition $Hg_{24}Na$ (Compt. rend. 88, 1335).

The views formerly held on the constitution of amalgams and particularly on the existence of definite amalgams of the nature of chemical compounds of mercury and the alloyed metal, have been profoundly modified by the study of those bodies by the methods of metallography (*v.* METALLOGRAPHY). The amalgams are found to be strictly analogous to other alloys, but their peculiar behaviour arises from the fact that they are frequently met with in a range of temperature which lies between the commencement of solidification and final complete crystallisation. It has been shown that a number of supposed compounds, of which the existence had been assumed on the ground that amalgams representing them took the form of homogeneous crystalline bodies, are not true compounds, whilst definite compounds of different composition have been found. Thus, in the case of sodium and potassium amalgams, the compounds Hg_4Na, Hg_2Na, $HgNa$, Hg_2Na_3, Hg_2Na_5, $HgNa_3$, and Hg_2K, HgK, Hg_3K, Hg_9K_2, and Hg_9K, have been recognised (Schüller, Zeitsch. anorg. Chem. 1904, 40, 385; Kurnakoff, *ibid.* 1900, 23, 439; Jaenecke, Zeitsch. physical. Chem. 1907, 58, 245).

The amalgams of bismuth, zinc, tin, and thallium are found not to contain any definite compounds (Pushin, Zeitsch. anorg. Chem. 1903, 36, 201; Heteren, *ibid.* 1904, 42, 129; Kurnakoff and Pushin, *ibid.* 1903, 30, 86).

'Ammonium amalgam' is prepared by acting on a saturated solution of ammonium chloride with sodium amalgam; the amalgam thus obtained soon breaks up into mercury, and ammonia and hydrogen gases. According to Wetherill (Amer. J. Sci. [2] 50, 160), this compound is not a true amalgam, as when an ammoniacal solution is electrolysed, the negative pole being a spongy plate impregnated with mercury, no amalgam is formed. Landolt (Zeitsch. f. Chem. [2] 5, 429) draws attention to the fact that ammonium amalgam does not reduce solutions of silver nitrate, ferric chloride, or cupric sulphate, as do sodium and potassium amalgams.

Seeley (Chem. News, 21, 265) has shown that on submitting ammonium amalgam to pressure, its volume diminishes in the same way as does that of a gas, and hence he considers that the ammonia and hydrogen exist in the amalgam as gas, and that the spongy mass is only a froth of mercury enclosing these gases.

Gellatlin (Zeitsch. f. Chem. [2] 5, 607) asserts that when ammonium amalgam, free from sodium, is placed in contact with phosphorus, phosphoretted hydrogen is evolved, and he infers that the hydrogen must be in the nascent state.

Pfeil and Lippmann (Compt. rend. 62, 426) state that trimethylamine hydrochloride also forms a spongy amalgam which quickly decomposes with evolution of hydrogen and formation of trimethylamine; saturated solutions of the hydrochlorides of aniline, conine, morphine, and quinine give off hydrogen only.

Electrical amalgam is made by melting together 1 part of zinc and 1 part of tin, and then adding 3 parts of mercury. An amalgam of cadmium is used in the construction of the cadmium standard cell; this amalgam and its electrical behaviour have been studied by F. E. Smith (Phil. Mag. February, 1910).

Silvering amalgams. For metals, 1 part of silver to 8 parts of mercury; for glass, 1 part each of lead and tin, 2 parts bismuth, and 4 parts mercury. The use of amalgams for silvering has been almost completely superseded by the use—in the case of glass—of chemically deposited silver, and in the case of metals by electro-plating.

Teeth fillings. 1. Copper precipitated from copper sulphate solution with zinc, washed with sulphuric acid containing a small quantity of mercuric nitrate, and amalgamated with twice its weight of mercury (Fletcher), has the property of softening with heat and hardening again after a few hours. It is a permanent filling, as the copper salts penetrate and preserve the tooth substance. It has the objection of staining the tooth, and is only used in posterior teeth. 2. A palladium amalgam is sometimes employed, but its rapidity of setting, intense black colour, and cost are against its general use. 3. An alloy of silver 68·5, tin 25·5, gold 5, and zinc 1 p.c. (Black); or silver 69·5, tin 25·5, gold 4, and zinc 1 p.c. (Tulloch), amalgamated with mercury, is extensively employed, as it has a good edge strength, and suffers little, if any, shrinkage. The shrinkage is the greatest difficulty to overcome in order to render alloys of permanent use for teeth filling, the object being to secure such a proportion of metals that the shrinkage of one may be overcome by the expansion of another, and so obtain a watertight plug. W. R.

AMALIC ACID *v.* ALLOXANTIN.

AMANITA MUSCARIA. *Fly agaric.* A poisonous fungus, used in Kamtschatka and Siberia as a narcotic and intoxicant, and, when steeped in milk, as a fly-poison. A narcotic organic base, *muscarine* $C_5H_{15}NO_3$, which is the hydrated aldehyde of betaine, has been isolated from it (Schmiedeberg and Harnack, J. 1876, 804).

The natural muscarine is like the artificial product in crystalline form, solubility, and composition of its platino- and auro-chlorides, and to a large extent in its physiological action, but unlike the artificial muscarine it does not induce paralysis of the intermuscular nerve-terminations in the frog, and myosis in the pupils of the eyes of birds (Nothnagel, Ber. 26, 801). It differs both in constitution and properties from anhydro- and *iso*-muscarine.

A green and red dye of composition $C_{29}H_{20}O_{10}$, and $C_{19}H_{18}O_6$ respectively, have also been isolated from it (Griffiths, Compt. rend. 130, 42).

AMARANTH *v.* AZO- COLOURING MATTERS.

AMARIN. Trade name for triphenyldihydroglyoxaline.

AMATOL. A mixture of 80 parts of ammonium nitrate with 20 parts of trinitrotoluene (T.N.T.). Used as an explosive. *See* EXPLOSIVES.

AMAZON-STONE. A bright-green variety of the potash-felspar microcline ($KAlSi_3O_8$). It is found in granitic rocks near Lake Ilmen in the Ural Mountains, at Pike's Peak in Colorado, and of very good quality in Madagascar. It is used to a limited extent as a gem-stone, and for making various small ornamental objects (*v.* FELSPAR). L. J. S.

AMBAR LIQUID *v.* BALSAMS.

AMBATOARINITE *v.* ANCYLITE.

AMBER or **SUCCINITE.** (*Bernstein*, Ger.) A fossil resin derived from the extinct conifer *Pinites succinifer* (Göppert), and found as irregular nodules in strata of Tertiary age, principally on the Prussian coast of the Baltic. The amber-bearing stratum lies partly below sea-level, and the amber washed out by the action of the waves is picked up on the sea-shore or won by dredging. Such 'strand-amber' was formerly collected farther west, as far as the coast of Holland, and isolated specimens are picked up on the east coast of England (Norfolk, Suffolk, and Essex). At the present time the bulk of Prussian or Baltic amber is obtained from pits and mines in the 'blue earth' in Samland, East Prussia. Here the production in 1907 amounted to 404,300 kilos. and in addition about 20,000 kilos was collected on the sea-shore.

Baltic amber differs from other fossil resins in containing succinic acid, which is present to the extent of 3 to 4 p.c. in perfectly transparent specimens, but reaching 8 p.c. in cloudy ('frothy') amber. It is therefore distinguished by the mineralogical name *succinite*, and in the trade the tendency is to apply the name 'amber' exclusively to Baltic amber. The composition is somewhat variable, averaging C, 79 p.c.; O, 10·5 p.c.; H, 10·5 p.c.; and corresponding approximately with the formula $C_{10}H_{16}O$. Sulphur is also present (0·26 to 0·42 p.c.), and some ash, usually about 0·2 p.c., but increasing in amount if the material encloses foreign matter. Amber is, however, not a simple resin; when heated, it gives oil of amber (*q.v.*) and other products, and by the action of solvents at least four different kinds of resin can be extracted from it. According to O. Helm, Baltic amber contains 17 to 22 p.c. of a resin (m.p. 105°) soluble in alcohol; 5 to 6 p.c. of a resin (m.p. 145°) insoluble in alcohol, but soluble in ether; 7 to 9 p.c. of a resin (m.p. 175°) insoluble in alcohol and ether, but dissolving in caustic potash; and 44 to 60 p.c. of insoluble bitumen.

Baltic amber is usually pale yellow, ranging to brown or reddish-brown in colour, and it varies from perfect transparency to opacity. The varying degrees of turbidity are due to the presence of vast numbers of microscopic air-bubbles. The enclosure of insects and fragments of wood and dirt in amber is well known, and points at once to the mode of origin of the material. According to differences in colour and transparency, various trade names are applied, such as 'clear,' 'flohmig,' 'cloudy,' 'bastard,' 'osseous' or 'bone,' and 'frothy.' The sp.gr. ranges from 1·05 to 1·10 (varying with the porosity); and the hardness is 2½, being rather higher than that of most other resins, which latter can be scratched with the finger-nail. The material is brittle and breaks with a conchoidal fracture. When cut with a knife, parings are not obtained, but only powder. It can be turned on the lathe and takes a good polish, being worked with whiting and water or rotten-stone and oil, and finished by friction with a flannel. When heated, amber begins to soften at about 150°, giving a characteristic odour; it melts at 350°–375°, that is, at a higher temperature than other resins, giving dense white fumes with a peculiar aromatic odour, and causing violent coughing. When rubbed it becomes negatively electrified (from the ancient name *electron*, for amber, the word 'electricity' is derived); and when rubbed vigorously it emits an aromatic odour, but does not become sticky like other resins. These characters serve to distinguish true amber from the more abundant copal; the latter is further usually clearer, lighter in colour, and more gummy in appearance.

In the trade the material is sorted into many grades suited for various purposes. The larger pieces of better quality ('work-stone') are cut into beads and other small personal ornaments, and are largely used for making the mouth-pieces of tobacco-pipes and cigar- and cigarette-holders. Smaller and impure fragments ('varnish') are melted down for the manufacture of amber varnish and lac; but in recent years such material is largely converted by the application of heat and hydraulic pressure into blocks of *pressed amber* or 'ambroid.' About 35,000 kilos of pressed amber is now produced annually from three times the amount of rough amber; it is cut for ornaments and smokers' mouth-pieces. Prices (current in 1908) for rough 'work-stone' vary, according to size and quality, from 11*l.* to 10*s.* per kilo, and for smaller, inferior material ('varnish') about 5*s.* per kilo. Pressed amber fetches 4*l.* to 5*l.* per kilo. The production and the trade in amber, as well as the literature of the subject, is almost exclusively German, though the finished articles are largely made in Vienna.

Other varieties of fossil resin closely allied to amber, but regarded as distinct from Prussian or Baltic amber (succinite), are the following:—

Beckerite (E. Pieszczek, 1880), a black resin occurring with Prussian amber.

Burmite, Birmite, or Burmese amber (F. Noetling, 1893), a dark reddish-brown, amber-like resin, which has long been mined in Upper Burma and used in China. It is found in large masses, one seen by the writer weighing 33½ lbs., whilst the largest piece of Prussian amber yet found weighs only 9·7 kilos (21¼ lbs.).

Chemawinite (B. J. Harrington, 1891), Cedarite (R. Klebs, 1897), or Canadian amber, found as pale yellow fragments the size of a pea to that of a walnut on the beach of Cedar Lake, near Chemahawin in Saskatchewan.

Delatynite (J. Niedźwiedzki, 1908), from Delatyn in the Galician Carpathians, differs from succinite in containing rather more carbon (79·93 p.c.), less succinic acid (0·74 1·67 p.c.), and no sulphur.

Gedrite (O. Helm, 1878), a bright, pale yellow resin found with Prussian amber, but differing from this in containing less oxygen and no succinic acid; m.p. 140°.

Glessite (O. Helm, 1881), also found with Prussian amber; it contains no succinic acid, but probably some formic acid; m.p. 200°.

Roumanite, Romanite, Rumanite, or Roumanian amber (O. Helm, 1891), a brownish-yellow to brown resin, found in Tertiary sandstone at several places in Roumania; it resembles Prussian amber in containing some succinic acid (0·3–3·2 p.c.), and is characterised by the relatively large amount of sulphur (1·15 p.c.); m.p. 300°.

Simetite, or Sicilian amber (O. Helm and H. Conwentz, 1886), a clear wine-red to garnet-red resin, remarkable for its beautiful green or blue fluorescence, found in the river Simeto and other parts of Sicily. It contains only 0·4 p.c. of succinic acid.

Stantienite (E. Pieszczek, 1880), a brown resin occurring with Prussian amber.

For several papers on amber and amber-like resins, by O. Helm and by P. Dahms, *see* Schr. natf. Ges. Danzig, vols. iv–xii (1878–1908). *See* also Max Bauer, Edelsteinkunde, 2nd edit. 1909, and English transl. (Precious Stones), by L. J. Spencer, 1904. L. J. S.

AMBER, OIL OF. When amber is heated it softens, fuses, and gives off succinic acid, water, oil, and a combustible gas. If the residue (colophony of amber) be more strongly heated, a colourless oil passes over. These oils, according to Pelletier and Walter (Ann. Chem. Phys. [3] 9, 89), have the composition of oil of turpentine. By distilling with water, a pale-yellow oil, having a strong odour and acrid taste, can be obtained. It blackens and thickens on exposure to air and heat, boils at 86°, and has a sp.gr. of 0·758 at 24°. One part of the rectified oil mixed with 24 parts of alcohol (0·830) and 96 of ammonia, forms *eau de luce*, a celebrated old perfume. By mixing 'eau de luce' with nitric acid, artificial musk is made. Its solution in alcohol was formerly considered as a specific for whooping-cough (*v.* also OILS, ESSENTIAL, and RESINS).

AMBER VARNISH *v.* VARNISH.

AMBERGRIS. (*Ambergris*, Fr.: *Ambra*, *Ambar*, Ger.) (J. Soc. Chem. Ind. 1890, 429.) Is found in the sea, near the coasts of tropical countries, and as a morbid product in the intestines of the cachalot or sperm whale (*Physeter macrocephalus*).

Ambergris is generally found in fragments, but pieces have been obtained weighing upwards of 270 lbs. Its sp.gr. ranges from 0·780 to 0·926 (0·780 to 0·896 Brande, 0·908 to 0·920 Pereira). If of good quality, it adheres like wax to the edge of a knife with which it is scraped, retains the impression of the nails, and emits a fat odoriferous liquid on being penetrated with a hot needle. It is generally brittle, but on rubbing it with the nail it becomes smooth like hard soap. Its colour varies from black to white. Its smell is peculiar, and not easily counterfeited. It melts at 62·2°, at 100° it is volatilised as a white vapour; on a red-hot coal it burns and is entirely dissipated. Water has no action on it; acids, except nitric acid, act feebly upon it; ether and the volatile oils dissolve it; so do the fixed oils, and also ammonia when assisted by heat; alcohol dissolves a portion of it.

The principal constituent of ambergris is *ambrein* (*q.v.*); its inorganic constituents are carbonate and phosphate of calcium, with traces of ferric oxide and alkaline chlorides.

Used by perfumers. The Chinese test its purity by scraping it upon boiling tea, in which it should wholly melt.

AMBERITE *v.* EXPLOSIVES.

AMBLYGONITE. Fluo-phosphate of aluminium and lithium $AlPO_4,LiF$, crystallising in the anorthic system. It is usually found as whitish cleavage masses much resembling felspar in appearance, from which it is distinguished by its higher sp.gr. 3·01–3·09 and chemical characters. It occurs in granitic rocks at Montebras in France, Cácares in Spain (with tin ore), Pala in California, &c. At each of the places named it has been mined for the preparation of lithium salts, the phosphate being a by-product. It contains about 10 p.c. of lithia. A variety in which the lithium is largely replaced by sodium has been found as greyish-white cleavage-masses in pegmatite near Canyon City in Fremont Co., Colorado, and named natramblygonite or fremontite. In another variety, known as montebrasite from Montebras in France, hydroxyl largely replaces the fluorine. The general formula for the mineral is then

$$(Li,Na)Al(F,OH)PO_4$$

L. J. S.

AMBREÏN. (*Ambreine*, Fr.; *Ambarstoff*, Ger.) Isolated by Pelletier and Caventou, by digesting ambergris in hot alcohol, sp.gr. 0·827. Ambreïn $C_{23}H_{40}O$, purified by repeated crystallisations from alcohol, is a white solid, separating in slender needles, m.p. 82°, which exhibit the phenomenon of superfusion for a long time even if sown with crystals. When warm and dry, it becomes highly electrified on slight rubbing. It has no optical activity, and is a neutral substance, insoluble in water, but soluble in most organic solvents, from which it does not crystallise out at all readily. When acted on by bromine in carbon tetrachloride solution, it gives an *octobromo-* derivative $C_{23}H_{32}OBr_8$, a white vitreous solid. Chlorine, under similar conditions, decomposes it. On warming ambreïn with phosphorus pentachloride, a white, amorphous mass of *pentachloro-ambrein* $C_{23}H_{35}OCl_5$ is obtained (Riban, Compt. rend. 1912, 154, 1729).

AMBRITE. A brown translucent resin, similar to retinite, found in association with New Zealand coal (*v.* RESINS).

AMEISINE. Trade name for aluminium formate.

AMENYL. Trade name for the *hydrochloride* of *methyl hydrastimide*. Forms yellowish needles, m.p. 227°. Soluble in hot water or alcohol.

AMERICAN COW or **MILK TREE WAX** *v.* WAX.

AMERICAN ELEMI *v.* OLEO-RESINS.

AMETHYST. A purple transparent variety of crystallised quartz (SiO_2), used as a gem-stone. So named, from ἀμέθυστος, 'not drunken,' owing to the ancient belief that the stone when worn as a charm prevented intoxication (*v.* QUARTZ). L. J S.

AMETHYST. Tetramethyl safranine and tetraamyl safranine are found in commerce under this name (*v.* AZINES).

AMETHYST, ORIENTAL, *v.* CORUNDUM.

AMIANTHUS (*Amiante,* Fr.) *Mountain flax* (*v.* ASBESTOS)

AMIDASE *v.* ENZYMES.

AMIDATION. The operation of introducing the amino group NH_2, as in the production of aniline from nitrobenzene by means of iron and hydrochloric acid.

AMIDE POWDER. An explosive similar to ordinary gunpowder, in which, in place of the sulphur, an ammonium salt is employed in combination with saltpetre, in such proportions that on ignition potassamide, volatile at high temperatures, is formed. This increases the useful effect of the explosive, which burns without residue (Gaens, Eng. Pat. 14412, 1885; J. Soc. Chem. Ind. 5, 678).

AMIDINES. Compounds containing amidogen and imidogen attached to the same carbon atom, *e.g.* *acetamidine* $CH_3{\cdot}C(NH)NH_2$; *benzamidine* $C_6H_5C(NH)NH_2$. They are formed by the action of amines on thio- amides or nitriles, or on the products formed by acting on the amides with phosphorus pentachloride, or by treating the cyanamides with the Grignard reagent (Adams and Beebe, J. Amer. Chem. Soc. 1916, 38, 2768).

AMIDOAZOBENZENE or **ANILINE YELLOW** *v.* AZO- COLOURING MATTERS.

AMIDOGENE. An explosive made by dissolving 73 parts of potassium nitrate and 1 part magnesium sulphate in one-third their weight of boiling water; 8 parts of ground wood charcoal, 8 parts of bran, and 10 parts of sulphur are added, and the whole is digested for two hours at 140°; it is then dried at 50° and made into cartridges (Gemperle, J. Soc. Chem. Ind. 3, 191; 1, 201; Biedermann's Chem. Tech. Jahrb. 7, 146).

AMIDOGUANIDINE *v.* HYDRAZINES.

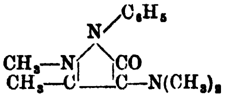
AMIDOL. Trade name for 2:4-diaminophenol hydrochloride, used as a photographic developer.

AMIDONAPHTHOLS *v.* AZO- COLOURING MATTERS.

AMIDONAPHTHOPHENAZINE *v.* AZINES.

AMIDOPHENOPHENANTHRAZINE *v.* AZINES.

AMIDOPYRINE (*Pyramidon*). Trade names for 4-dimethylamino antipyrine.



Prepared by treating an acid solution of antipyrine with sodium nitrite, reducing the nitroso-antipyrine to amino-antipyrine, condensing with benzaldehyde, and decomposing the benzylidene derivative with hydrochloric acid. The product on methylation yields amidopyrine.

AMINES. Amines or 'ammonia bases' may be regarded as substances derived from ammonia by the substitution of hydrocarbon radicals for hydrogen. They may also be looked upon as derived from hydrocarbons by the replacement of one or more hydrogen atoms by NH_2 or its alkyl substitution products NHR or NRR′. The definition of the term may be taken to include alkyl derivatives of hydrazine and hydrazoic acid, and compounds such as nitrosamines diazo-compounds; also others which contain nitrogen linked to nitrogen or elements other than carbon, as well as to alkyl- residues. It also includes compounds in which the nitrogen forms part of a ring, as in pyridine, pyrrol, and their derivatives, among which the alkaloids may be mentioned. The majority of these more complex substances are treated of in detail in special articles (*see* arts. AZO-COLOURING MATTERS; AZINES; BONE OIL; QUINOLINE, &c.), and come within the scope of this only in so far as they possess the general characteristics of the ammonia bases.

Amines are classed as primary, secondary, or tertiary, according as one, two, or three of the hydrogen atoms of ammonia have been replaced by alkyl or aryl groups. Thus the general formula of the primary amines is NH_2R, of the secondary amines NHRR′, and of the tertiary amines NRR′R″, where R, R′, and R″ may be identical or represent different radicals. The reactions of the amines differ to some extent according as the substituting radicals are (1) all aliphatic; (2) mixed aliphatic and aromatic, with the nitrogen attached to the aliphatic residue, as in benzylamine; (3) mixed aliphatic and aromatic, with the nitrogen attached to a carbon atom of the benzene ring, as in methyl aniline; and (4) pure aromatic amines such as aniline itself, di- and tri-phenylamine, and their homologues. Substances of groups (1) and (2) will be referred to here as aliphatic and aromatic amines respectively, and those of groups (3) and (4) as aromatic amino- compounds. Aromatic amino- compounds serve as the starting materials in many of the different branches of the dyeing industry, and are prepared artificially in large quantities (*see* arts. ANILINE; AZO- COLOURING MATTERS; TRIPHENYLMETHANE COLOURING MATTERS; DIPHENYLAMINE, &c.).

With the important exception of the vegetable alkaloids, the amines are not widely distributed in nature, though some of the lower members of the fatty series (methylamines) occur in plants and in the blood of some animals. They are, however, found as decomposition products of animal and vegetable organisms, and of mineral substances. Thus the methylamines are found in herring brine and in decomposing fish. Others, chiefly diamines, are found in certain pathological conditions of the urine, and as decomposition products of the animal tissues (ptomaines). The decomposition of proteins give rise to large numbers of amino-acids. Aniline was first isolated as a product of the distillation of indigo, and it and its homologues as well as other bases are present in the distillates from bone oil (Dippel's oil), and of coal tar. A mixture of fatty amines is obtained in the dry distillation of the residues in the beet-sugar industry, and this, under the name of 'trimethylamine,' of which it contains about 5 p.c., is used in France for the preparation for industrial purposes of methyl chloride; on account of the greater solubility of its hydrochloride, it has also been used instead of ammonia in the preparation of potassium carbonate, in a manner analogous to the Solvay method for the preparation of sodium carbonate, but the process does not seem to have been commercially successful.

General methods of preparation.

1. *By action of ammonia or its alkyl derivatives on substitution products (generally haloid or hydroxyl derivatives) of hydrocarbons.*

The method first described by Hofmann (Phil. Trans. 1850, 1, 93; 1851, 2, 357), of heating alkyl halides (preferably bromides or iodides) with ammonia, is available for the preparation of primary, secondary, and tertiary amines of the fatty series, and if aniline is substituted for ammonia, for the preparation of secondary, tertiary, and aromatic amino- compounds. Quaternary ammonium compounds are also formed in the reactions, which may be represented as follows:—

$$\mathrm{NH_3 + RBr = NH_2R{\cdot}HBr}$$
$$\mathrm{NH_2R + R'Br = NHRR'{\cdot}HBr}$$
$$\mathrm{NHRR' + R''Br = NRR'R''{\cdot}HBr}$$
$$\mathrm{NRR'R'' + R'''Br = NRR'R''R'''Br}$$

The reaction will take place, though only very slowly, in aqueous solution, more quickly in alcoholic solution, and best on heating in alcoholic solution in sealed tubes at 100°. The products obtained may contain haloid salts of one or all of the possible amines, and of the quaternary bases, and the proportions vary with the conditions of experiment (Werner, Chem. Soc. Trans. 1918, 113, 899; 1919, 115, 1010). On distilling the product with excess of alkali a mixture of the three amines is obtained; the three amines may be separated from the mixture by making use of their different modes of reaction with oxalic ester, the chlorides of aromatic sulphonic acids, Grignard's reagent, acetic anhydride, or acetyl chloride, which are dealt with below. The three ethyl amines have been separated by fractional distillation (Garner and Tyrer, Chem. Soc. Trans. 1916, 109, 174. *Cf.* also Price, J. Soc. Chem. Ind. 1918, 37, 82.

In the preparation on the large scale of secondary and tertiary aromatic amino- compounds, *e.g.* dimethylaniline, the primary amine is heated under pressure directly with the alcohol and hydrochloric or sulphuric acid at 180°–200°. Here the alkyl group is exchanged directly for hydrogen without the intermediate separation of the alkyl halide. The presence of other negative groups in the benzene molecule increases the ease with which the NH_2 group can displace halogen groups. Thus the chlorine atoms of chlorbenzene can be replaced by NH_2 groups by the action of ammonia if the benzene ring also contains NO_2 groups. A catalytic method of preparing mono- and di-methylaniline, in which the vapours of methyl alcohol and aniline are passed over aluminium oxide at 400°–430°, is described by Mailhe and de Godon (Compt. rend. 1918, 166, 467).

Amines may also be obtained by heating zinc ammonium chloride with alcohols at 250°–260° (Merz and Gasiorowski, Ber. 1884, 17, 623).

Alcohols or phenols will react with ammonia or its alkyl derivatives on heating in the presence of zinc chloride, calcium chloride, or other catalytic agent (Merz and Weith, Ber. 1880, 13, 1298; Merz and Mueller, Ber. 1886, 19, 2901).

Mixtures of the vapours of alcohol and ammonia or primary amine led through tubes containing finely divided thoria or tungsten oxide at 360° give amines (Sabatier and Mailhe, Compt. rend. 1908, 148, 898).

Sodamide or its alkyl substitution products may be used instead of ammonia in the case of aliphatic amines.

$$\mathrm{NH_2Na + CH_3Cl = NH_2{\cdot}CH_3 + NaCl}$$

(Lebeau, Compt. rend. 1905, 140, 1042; Chablay, Compt. rend. 1905, 140, 1262). *Cf.* O. Matter, D. R. PP. 301450, 301832. Sodamide will also react with anhydrous sulphuric esters of the aliphatic series, and with aromatic sulphonic acids to give primary amines (Jackson and Wing, Ber. 1886, 19, 902; Titherley, Chem. Soc. Trans. 1901, 79, 399).

By heating ammonium chloride with a concentrated solution of formaldehyde under pressure, methylamine, dimethylamine, and trimethylamine are successively produced (Eschweiler, D. R. P. 80520, 1893).

2. *By reduction of nitrogen-containing substances.*

Primary amines may be obtained by the reduction of nitro- compounds, nitroso- compounds, oximes, hydrazones, azo- and hydrazo- compounds, amides and amidines, and nitriles. Since the nitro- compounds of aromatic hydrocarbons are easily prepared by direct nitration, the reduction of nitro- compounds is by far the most generally used method for the preparation of aromatic primary amines. Zinin in 1842 prepared aniline from nitrobenzene, by the action of alcoholic ammonium sulphide, and this method is still in use for the reduction of the dinitrobenzenes to the nitroanilines. On the commercial scale, as for instance in the preparation of aniline, iron and water with some hydrochloric acid is usually employed as the reducing agent. Another method for the reduction of nitro- compounds, nitriles, oximes, and hydrazones, consists in heating in a stream of hydrogen in the presence of finely divided nickel or copper (Sabatier and Senderens, Compt. rend. 1902, 125, 225). A great deal of work on this method, resulting in a large number of patents, has been carried out. With a copper catalyst obtained by reducing the carbonate, formate, oxalate, or nitrate by hydrogen or carbon monoxide below red heat, reduction of a nitro- compound is effected by hydrogen at a temperature of 200° C. or less. Higher temperatures lead to impure products and to poisoning of the catalyst (Badische Anilin und Soda Fabrik, D. R. PP. 263396, 1914; 282568, 1915). Other contact agents are described by the same patentees in Eng. Pat. 5692, 1915. According to D. R. P. 282492, 1915 (Meister, Lucius, and Bruning) a quantitative yield of aniline is obtained by passing nitrobenzene, steam, and hydrogen at 120° C., over finely divided nickel. In Eng. Pat. 6409, 1915 (Badische Anilin und Soda Fabrik), the reduction of nitrobenzene by carbon monoxide in presence of steam and a contact agent, is described.

Nitro- compounds may be reduced to primary amines electrolytically, in aqueous or alcoholic acid solution, at zinc, lead, tin, copper, or mercury cathodes, with a current density of 0·18 amp /sq. cm. Tin and lead are particularly effective if they are present on the cathode in a spongy state (C. F. Boehringer and Sohne, D. R. P. 116942, 1900).

The reduction of nitroso- compounds, oximes, and hydrazones, though often useful in the laboratory for preparing special amino-compounds, is seldom of use on the large scale. The reducing agents used are, for nitroso- compounds, such as nitrosophenol, sulphuretted hydrogen in presence of ammonia; for oximes and hydrazones, sodium amalgam and acetic acid.

The reduction of azo- compounds, which takes place according to the equation

$$R{-}N{=}N{-}R'+2H_2=R{-}NH_2+NH_2{\cdot}R'$$

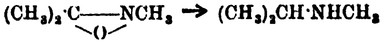
is mainly used in the production of aromatic primary diamines (*cf.* *p*-phenylenediamine, but can be used for the production of aminophenols or their derivatives. Thus (D. R. P. 48543), by diazotising one molecule of *p*-aminophenetol and coupling with phenol the azo- compound $C_2H_5OC_6H_4{-}N_2{-}C_6H_4OH$ is produced, and this on ethylation and reduction gives two molecules of *p*-aminophenetol. The usual reducing agents for azo- compounds are stannous chloride, zinc-dust and water or acetic acid, and sodium hyposulphite ($Na_2S_2O_4$).

Amides, amidines, and nitriles are best reduced by sodium and alcohol.

$$R{\cdot}CO{\cdot}NH_2 \rightarrow R{\cdot}CH_2NH_2$$
$$R{\cdot}CH(NH){\cdot}NH_2 \rightarrow R{\cdot}CH_2NH_2+NH_3$$
$$R{\cdot}CN \rightarrow R{\cdot}CH_2{\cdot}NH_2$$

The formation of methylamine by the reduction of alkali cyanides and ferrocyanides with hydrogen in the presence of colloidal palladium has been patented (Riedel, 1913, D. R. P. 264528). For the catalytic reduction of hydrocyanic acid see Barratt and Titley, Chem. Soc. Trans. 1919, 115, 902.

Secondary amines may be produced by reduction of the *N*-esters of the oximes (Goldschmidt, Ber. 1892, 25, 2594; Dunstan and Goulding, Chem. Soc. Trans. 1897, 71, 573; 1901, 79, 628) or of the *iso*nitriles, or of the condensation products formed by the action of primary amines on aldehydes.



$$(CH_3)_2{\cdot}C\underset{O}{\text{——}}NCH_3 \rightarrow (CH_3)_2CH{\cdot}NHCH_3$$

$$R{-}N:C \rightarrow R{\cdot}NH{\cdot}CH_3$$
$$R{\cdot}N:CH{\cdot}R' \rightarrow RNH{\cdot}CH_2R'$$

A special case of the third reaction—the methylation of primary amines by means of formaldehyde, without isolation of the intermediate condensation product—is of great technical importance. According to a patent of F. Bayer & Co. (D. R. P. 287802, 1916), any primary amine may be methylated by being heated to a high temperature with formaldehyde in presence of some reducing agent other than formaldehyde or formic acid. A process for the preparation of methylaniline by the action of formaldehyde on aniline has been described by G. T. Morgan (Eng. Pat. 18081, 1915). The mechanism of the reactions involved in methylation by formaldehyde has been investigated by E. A. Werner (Chem. Soc. Trans. 1917, 111, 844).

3. *From amides by the action of bromine and potash.* (Hofmann, Ber. 1882, 15, 762.)

This reaction is mainly applicable to the preparation of primary fatty amines, and gives good yields only with the lower members of the series. The first product of the reaction is a bromamide, and this on further treatment with potash gives potassium bromide and an *iso*cyanate, which is saponified, giving an amine and a carbonate, the alkyl group being transferred from the carbon to the nitrogen atom, as in the 'Beckman rearrangement' (Mohr, J. pr. Chem. 1906, [2] 73, 177, 228).

$$CH_3{\cdot}CONH_2+KOH+Br_2$$
$$=CH_3{\cdot}CONHBr+KBr+H_2O$$
$$CH_3{\cdot}CONHBr+KOH=CH_3{\cdot}NH_2+CO_2+KBr$$

Azides on boiling with alcohol or water, and subsequent treatment with conc. HCl give amines.

$$R{\cdot}CO{\cdot}N_3+C_2H_5{\cdot}OH=RNH{\cdot}COOC_2H_2+N_2$$
$$R{\cdot}NH{\cdot}COOC_2H_5+H_2O$$
$$=RNH_2+CO_2+C_2H_5OH$$

(Curtius, Ber. 1894, 27, 779; 1896, 29, 1166; Forster, Chem. Soc. Trans. 1909, 95, 433).

4. *From compounds containing imido (or amido) groups in which one atom of hydrogen is replaceable by alkali metals.*

(*a*) From *iso*cyanates, *iso*thiocyanates, and *iso*cyanides.

Alkyl *iso*cyanates (prepared from metallic *iso*cyanates and alkylhaloids) are hydrolysed by alkalis (Wurtz, Annalen, 1849, 71, 330).

The interest of this method is mainly historical, since it led to the discovery of the amines by Wurtz in 1848. Primary amines are the chief product, but secondary and tertiary amines are also formed in small quantities.

$$C_2H_5NCO+H_2O=C_2H_5{\cdot}NH_2+CO_2$$

Alkyl *iso*thiocyanates and *iso*cyanides are hydrolysed by treatment with concentrated hydrochloric acid.

$$C_2H_5NCS+H_2O=C_2H_5{\cdot}NH_2+COS$$
$$C_2H_5NC+H_2O=C_2H_5{\cdot}NH_2+HCOOH$$

(*b*) Phthalimide, on treatment with alcoholic potash, gives potassium phthalimide, and this gives an alkyl derivative on treatment with alkyl iodide, which on hydrolysis with fuming HCl yields a primary amine.

$$C_6H_4(CO)_2NK+RI=C_6H_4(CO)_2NR+KI$$

$$C_6H_4(CO)_2NR+2H_2O=C_6H_4(COOH)_2+NH_2R$$

(Gabriel, Ber. 1887, 20, 2224; 1891, 24, 3104). Gabriel and Ohle (Ber. 1917, 50, 804, 819) find that alkylene oxides will react with potassium phthalimide with the ultimate formation of aminohydroxy compounds.

(*c*) A similar method, available for the preparation of secondary amines from primary, is due to Hinsberg (Annalen, 1891, 179, 265). The sodium derivative of a substituted benzenesulphonamide (derived from the action of benzene sulphonylchloride on a primary amine) is treated with an alkyl iodide, and the product hydrolysed with hydrochloric acid at 120°–180°.

$$C_6H_5SO_2{\cdot}NR{\cdot}Na \rightarrow C_6H_5SO_2{\cdot}NRR' \rightarrow NHRR'$$

Johnson and Ambler use toluene-ω-sulphonamides in the same way (J. Amer. Chem. Soc. 1914, 36, 372). E. Fischer finds that a better yield of the amine is obtained by treating the disubstituted sulphonamide with hydriodic acid and phosphonium iodide (Ber. 1915, 48, 93).

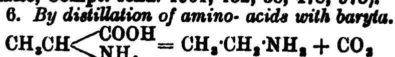
(*d*) The derivatives of the amides of the carboxylic acids, though less suitable, on account of their less acidic properties, can be used in the same way as the derivatives of the sulphonamides (Titherley, Chem. Soc. Trans. 1901, 79, 399).

(5) *From compounds which certain substances form with alkyl haloids.*

(*a*) Hexamethylene tetramine, formed by the action of ammonia on formaldehyde, gives addition compounds of the type $C_6H_{12}N_4{\cdot}RI$ with alkyl iodides. These on treatment with HCl and alcohol are decomposed, giving primary amines (Delépine, Compt. rend. 1897, 124, 292; Ann. Chim. Phys. 1898, [7] 15, 508).

(*b*) Magnesium alkyl iodides form addition compounds with phenyl *isocyanate*; these, on treatment with water are converted into anilides, which yield amines on saponification (Blaise, Compt. rend. 1901, 132, 38, 478, 978).

6. *By distillation of amino- acids with baryta.*



$$CH_3CH\left\langle\begin{matrix}COOH\\NH_2\end{matrix}\right. = CH_3{\cdot}CH_2{\cdot}NH_2 + CO_2$$

7. *Aliphatic primary and secondary amines may be obtained by the action of potash on the p-nitroso- derivatives of secondary and tertiary aromatic amino- compounds.*

$$NO{\cdot}C_6H_4{\cdot}N(CH_3)_2 + KOH$$
$$= NO{\cdot}C_6H_4{\cdot}OK + N(CH_3)_2H$$

$$NO{\cdot}C_6H_4{\cdot}NHCH_3 + KOH$$
$$= NO{\cdot}C_6H_4{\cdot}OK+NH_2{\cdot}CH_3$$

8. *Tertiary amines can be obtained by heating primary and secondary bases with excess of potassium alkyl sulphate.*

$$RR'NH+CH_3OSO_3K=RR'NCH_3+HOSO_3K$$

General Properties.

The amines of the aliphatic series are volatile inflammable substances, the lower members being gases or liquids with low boiling-points, very soluble in water and strongly alkaline to litmus; the density of the liquid members of the series is about 0·75 that of water, and increases slightly with increase in the molecular weight. Their basicity, measured by the conductivity method, is considerably greater than that of ammonia, and they will saponify esters and precipitate oxides from the salts of many of the heavy metals. They have an ammoniacal and fishy odour. The smell, inflammability, boiling-point, and solubility in water become less with increase in the molecular weight, and the highest known members are odourless solids at ordinary temperatures. They react with moist air with formation of

ALIPHATIC AMINES.

Alkyl groups	Primary compounds			Secondary compounds		Tertiary compounds	
	M pt.	B pt	Sp.gr.	B.pt.	Sp.gr.	B.pt.	Sp.gr.
Methyl	—	−6·7°	0·699 (−11°)	+7°	0·686 (−6°)	+3·5°	0·662 (−5°)
Ethyl	−83·8°	+19°	0·708 (−2°)	56°	0·711 (+15°)	90°	0·735 (+15°)
Propyl	—	49°	0·728 (0°)	110°	0·738 (20°)	156°	0·771 (0°)
iso-Propyl	—	32°	0·690 (18°)	84°	0·724 (15°)	—	—
prim. n-Butyl	—	77·8°	0·742 (15°)	160°	—	216·5°	0·791 (0°)
iso-Butyl	—	66°	0·735 (15°)	136°	—	187°	0·785 (21°)
sec. Butyl	—	63°	0·718 (20°)	—	—	—	—
tert. Butyl	—	43·8°	0·698 (15°)	—	—	—	—
prim. n-Amyl	—	104°	0·766 (19°)	—	—	—	—
iso-Amyl	—	95°	0·750 (18°)	187°	0·782 (0°)	235°	—
tert. Butyl-methyl	—	82°–83°	—	—	—	—	—
sec. n-Amyl	—	90°–91°	0·749 (20°)	—	—	—	—
sec. iso-Amyl	—	83°–84°	0·757 (18·5°)	—	—	—	—
tert. Amyl	—	78·5°	0·748 (15°)	—	—	—	—
prim. n-Hexyl	—	129°	—	—	—	260°	—
„ „ Heptyl	—	153°	0·777 (20°)	—	—	—	—
„ „ Octyl	—	175°–177°	0·777 (26·8°)	297°	—	366°	—
„ „ Nonyl	—	190°–192°	—	—	—	—	—
„ „ Decyl	+17	216°–218°	—	—	—	—	—
„ „ Undecyl	15°	232°	—	—	—	—	—
„ „ Duodecyl	27°	248°	—	—	—	—	—
„ „ Tridecyl	27°	265°	—	—	—	—	—
„ „ Tetradecyl	37°	162° (15 mm.)	—	—	—	—	—
„ „ Pentadecyl	36·5°	298°–301°	—	—	—	—	—
„ „ Hexadecyl	45°	187° (15 mm.)	—	—	—	—	—
„ „ Heptadecyl	49°	335°–340°	—	—	—	—	—

HOMOLOGUES OF ANILINE.

Primary aromatic amino- compounds						
Formula	Popular name	Systematic name	M.pt.	B.pt.	Sp. gr.	M. pt. of mon-acetyl deriv.
$C_6H_5 \cdot NH_2$	aniline	aminobenzene	−8°	183°	1·024 (16°)	115°
$CH_3 \cdot C_6H_4 \cdot NH_2$	ortho toluidine	1-methyl-2-aminobenzene	—	199°	0·999 (20°)	110°
	meta „	1-methyl-3-aminobenzene	—	199°	0·998 (25°)	65·5°
	para „	1-methyl-4-aminobenzene	+42·8°	198°	—	153°
$(CH_3)_2C_6H_3 \cdot NH_2$	1-2-3 ortho xylidine	1 : 2-dimethyl-3-aminobenzene	—	223°	0·991 (15°)	134°
	1-2-4 „ „	1 : 2-dimethyl-4-aminobenzene	+49°	226°	1·076 (17°)	99°
	1-3-2 meta „	1 : 3-dimethyl-2-aminobenzene	—	215°	—	176·5°
	asymm. meta xylidine	1 : 3-dimethyl-4-aminobenzene	—	215°	0 918 (25°)	129°
	symm. meta xylidine	1 : 3-dimethyl-5-aminobenzene	—	223°	0·972 (15°)	140·5°
	para xylidine	1 : 4-dimethyl-2-aminobenzene	+15·5°	215°	0·980 (15°)	139·5°
$C_2H_5 \cdot C_6H_4 \cdot NH_2$	para amino ethyl benzene	1-ethyl-4-amino-benzene	−5°	214°	0·975 (22°)	94·5°
$(CH_3)_3C_6H_2 \cdot NH_2$	mesidine	1 : 3 : 5-trimethyl-2-aminobenzene	—	233°	—	216°
	pseudo-cumidine	1 : 2 : 4-trimethyl-5-aminobenzene	+68°	234°	—	164°
$(C_2H_5 \cdot CH_2)C_6H_4 \cdot NH_2$	para amino propyl benzene	1-propyl-4-aminobenzene	—	225°	—	—
$(CH_3)_2CH\ C_6H_4 \cdot NH_2$	cumidine	1-*iso*propyl-4-aminobenzene	—	218°	—	102·5°
$(CH_3)_4C_6H \cdot NH_2$	prehnidine	1 : 2 : 3 · 4-tetramethyl-5-aminobenzene	+70°	260°	—	172°
	isoduridine	1 : 2 : 3 : 5-tetramethyl-4-aminobenzene	+24°	255°	0·978 (24°)	215°
$(CH_3)(C_3H_7)C_6H_3 \cdot NH_2$	carvacrylamine	1-methyl-4-*iso*propyl-2-aminobenzene	—	241°	0 944 (24°)	72°
	thymylamine	1-methyl-4-*iso*propyl-3-aminobenzene	—	230°	—	112·5°
$(CH_3)_2CH\ CH_2\ C_6H_4\ NH_2$	para amino *iso*butyl benzene	1-*iso*butyl-4-aminobenzene	+17°	230°	0·937 (25°)	170°
$(CH_3)_5C_6 \cdot NH_2$	amino pentamethyl benzene	pentamethyl aminobenzene	152°	278°	—	213°
$C_5H_{11} \cdot C_6H_4 \cdot NH_2$	amino *iso*amyl benzene	—	—	260°	—	—
$C_8H_{17} \cdot C_6H_4 \cdot NH_2$	para amino octyl benzene	1-octyl-4-aminobenzene	+19·5°	310°	—	93°
$C_{16}H_{33} \cdot C_6H_4 \cdot NH_2$	amino cetyl benzene	hexadecyl aminobenzene	53°	255° (14 mm.)	—	104°
$C_{18}H_{37} \cdot C_6H_4NH_2$	amino octadecyl benzene	octadecyl aminobenzene	61°	274 (15 mm)	—	—

carbonates. Aromatic amines (benzylamine and its homologues) closely resemble the aliphatic amines, but are not quite so strongly basic in character, owing to the presence of the negative phenyl group. The aromatic amino-compounds (aniline and its homologues) are less basic than ammonia, and the basicity diminishes with increase of the number of phenyl-groups attached to the nitrogen atom. Thus the salts of diphenylamine are hydrolysed by water to a greater extent than those of aniline, whilst triphenylamine is a neutral body and forms no salts with acids. Comparatively few amines are known which contain only aromatic groups; of these aniline and diphenylamine are prepared on the large scale in the dyeing industry, as well as many secondary and tertiary amino compounds containing both fatty and aromatic groups.

The aromatic amines are much more easily substituted by halogens, the nitro group and the sulphonic group than the hydrocarbons from which they are derived, and the substituted derivatives obtained are of great importance in the dye industry. In substituting with halogens or nitric acid it is often necessary to protect the amino group by acetylation, the acetyl group being subsequently removed. The purely aliphatic amines find little use outside synthetical chemistry. Some are used in the preparation of drugs; they have also been used (as well as derivatives of aromatic amines) as catalysts in the vulcanisation of rubber (Twiss, J. Soc. Chem. Ind. 1917, 780).

The above lists of the chief homologues of methylamine and aniline are taken from Meyer and Jacobsen's Lehrbuch der Organischen Chemie.

All classes of amines form addition products with acids, containing one molecule of base to one molecule of monobasic acid. Compounds containing three molecules of HCl to one of amine have also been obtained (Korczynski, Ber. 1908, 41, 4379). The picrates are specially characteristic, and are used for the identification of the amines, as are also the double salts with platinum and gold chlorides, which have the general formulæ $B_2H_2PtCl_6$ and $BHAuCl_4$ respectively. Many aliphatic amines form hydrates with one molecule of water of crystallisation. Double salts with mercuric chloride and stannous and stannic chlorides (Druce, Chem. Soc. Trans. 1918, 113, 715), and with silver salts, crystallise well, and organic analogues of ammonium pyrophosphate and arsenate are known, but are not very stable (Brisac, Bull. Soc. chim. 1903, [3] 29, 591). With alkyl halides they form quaternary ammonium compounds of the type $NRR'R''R'''I$, where $RR'R''R'''$ may be the same or different radicals. In cases where these radicals are all different, the substances are capable of existing in two enantiomorphous optically active forms, and a number of these have been isolated. Enantiomorphic compounds of the type $RR'R''N{=}O$ have also been isolated (Meisenheimer, Ber. 1908, 41, 3966; Annalen, 1911, 385, 117). The quaternary ammonium compounds, unlike their inorganic analogues, are not decomposed on boiling with potash; on heating alone they give tertiary amines and alkyl halides. The corresponding bases are obtained from their halides by treatment with moist silver oxide; they are strongly alkaline to litmus, and the solutions generally decompose easily on evaporation, but some of the aliphatic members have been obtained crystalline by evaporation *in vacuô*. The rate of formation of quaternary ammonium compounds from tertiary amines and alkyl haloids is found to vary greatly with the constitution of the reacting substance and the nature of the solvent (Menschutkin, Zeitsch. physikal. Chem. 1890, 6, 41; Wedekind, Ber. 1899, 32, 511; Annalen, 1901, 318, 90; Preston and Jones, Chem. Soc. Trans. 1912, 101, 1930; Thomas, Chem. Soc. Trans. 1913, 103, 594).

The formation of quaternary ammonium compounds by addition of excess of methyl iodide to an amine gives a quantitative method for the determination of the number of replaceable hydrogen atoms in the substance. Analysis of the original compound and of its quaternary methyl derivative gives the number of methyl groups which have entered into the molecule.

Compounds containing five hydrocarbon radicals attached directly to nitrogen were for a long time thought to be incapable of existence. Such compounds have now been isolated by Schlenk and Holtz (Ber. 1916, 49, 603; 1917, 50, 274).

With several reagents, the different classes of amines show different reactions, and separation and purification of the amines formed in many of the methods above referred to may be carried out by making use of such differences. Primary and secondary amines sometimes give similar reactions, whilst tertiary amines are more stable.

Reactions.

1. *With nitrous acid.*

Primary amines, on boiling with potassium or sodium nitrite in acid solution, give alcohols or phenols with evolution of nitrogen.

$$RNH_2+HONO = ROH+N_2+H_2O$$

In many cases where a primary alcohol would be expected a mixture of primary and secondary alcohols is obtained (Henry, Compt. rend. 1907, 145, 899, 1247).

Secondary amines give nitrosamines, which on boiling with conc. HCl are again transformed into the original amines.

$$RR'NH+HONO = RR'N{\cdot}NO+H_2O$$
$$RR'N{\cdot}NO+2HCl = RR'NH{\cdot}HCl+NOCl$$

Tertiary amines do not react.

Primary aromatic amino- compounds react differently if their solutions are kept cooled. They give diazo- compounds according to the following equation:—

$$RNH_2,HCl+HONO = RN:NCl+2H_2O.$$

This reaction is of the greatest importance, for the diazo- compounds are very unstable, and on treatment with various substances either form substitution products of benzene hydrocarbons with evolution of nitrogen, or retain the nitrogen and form azo- compounds, which are the parent substances of the azo- dyes. Thus, if the diazo- compound be boiled with water, alcohol, cuprous chloride, bromide, or cyanide, phenol, benzene, chlor- brom- or cyan- derivatives respectively are produced. If the diazo- compound is treated with a substance containing a phenol or aromatic amino- group, a coloured substance is formed which is capable of fixing itself as a dye on a fabric. Compounds derived from unsubstituted amines have only a limited application for dyeing purposes, as they are generally insoluble in water; the sulphonic acids derived from them are, however, generally soluble, and are used extensively (*see* art. AZO-COLOURING MATTERS). The reactions are expressed by the following equations:—

$$C_6H_5N_2Cl+C_6H_5OH=C_6H_5N:NC_6H_4OH+HCl$$
$$C_6H_5N_2Cl+C_6H_5N(CH_3)_2$$
$$=C_6H_5N:NC_6H_4N(CH_3)_2+HCl$$

Tertiary aromatic compounds, such as dimethylaniline, react with nitrous acid to form *p*-nitroso compounds, where the nitroso nitrogen is attached to the carbon of the benzene ring in the para- position to the substituted amino- group. These are highly coloured substances, and serve as intermediate compounds in the production of certain colouring matters (methylene blue, &c.), which are used in the colour industry. On treatment with caustic potash they give secondary amines and salts of nitroso phenol.

Since nitrites of primary, secondary, and tertiary amines have been isolated (Wallach, Chem. Zentr. 1907, ii. 54; Neogi, Chem. Soc. Trans. 1912, 101, 1610; and 1914, 105, 1270), it is probable that in all the above-mentioned reactions the nitrite of the amine is formed as an intermediate product.

2. *With chlorides of aromatic sulphonic acids.*

Primary and secondary amines in strong alkaline solution are converted into amides by shaking with chlorides of aromatic sulphonic acids; tertiary amines do not react. Of these amides, $Ph{\cdot}SO_2NHR$ and $PhSO_2NRR'$ respectively, the first only are soluble in dilute alkalis with formation of salts. The primary and secondary amines can be regenerated from the amides by boiling with conc. HCl or H_2SO_4 at 120°–150° (Hinsberg, Ber. 23, 2963; Annalen, 1891, 265, 178). E. Fischer (Ber. 1915, 48, 93) recommends hydrolysis by hydriodic acid and phosphonium iodide. These reactions provide the only generally applicable method for separating mixtures of primary, secondary, and tertiary amines.

3. *With acetyl chloride or acetic anhydride.*

Primary and secondary amines give, as a rule, acetyl derivatives which are insoluble in cold water; tertiary amines either do not react, or form soluble acetates and hydrochlorides. The primary and secondary amines may be regenerated by hydrolysis of the acetyl derivatives. Since the velocity of the formation of the acetyl derivative of the primary is much greater than that of the secondary amine, a method based on this difference in property has been used to separate the two (Menschutkin, Chem. Zentr. 1900, 1, 1071; Potozki and Gwosdow, *ibid.* 1903, ii. 339).

The action of benzoy chloride is similar to that of acetyl chloride.

4. *With oxalic ester.*

Several of the aliphatic primary and secondary amines react with ethyl oxalate, the former giving solid diamides and the latter liquid oxamic esters. Tertiary amines do not react. Primary and secondary amines are regenerated by boiling with potash (Hofmann, Ber. 1870, 3, 109, 776; Duvillier and Buisine, Ann. Chim. Phys. [5] 23, 299). Hofmann used these reactions for the separation of the three ethylamines, and it has been used since in other cases.

5. *With magnesium methyl iodides.*

Primary amines react, giving two molecules of methane for every molecule of amine:

$$RNH_2+2MeMgI = RN(MgI)_2+2CH_4$$

Secondary amines react in a similar manner, but give one molecule of methane for every molecule of amine:

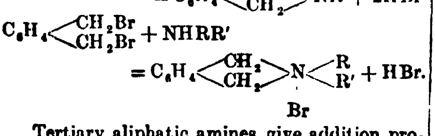
$$RR'NH+CH_3MgI = RR'NMgI+CH_4$$

Tertiary amines either do not react or they form addition compounds with the reagent (Sudborough and Hibbert, Chem. Soc. Trans. 1909, 95, 477; Hibbert and Wise, Chem. Soc. Trans. 1912, 101, 344).

6. *With o-xylylene bromide.*

Primary amines react, giving two molecules of HBr and liquid derivatives of *o*-xylyleneimine (dihydro*iso*indol)

Secondary amines react, giving crystalline quaternary ammonium bromides and one molecule of HBr:



$$C_6H_4<\begin{array}{l}CH_2Br\\CH_2Br\end{array}+NH_2R = C_6H_4<\begin{array}{l}CH_2\\CH_2\end{array}>NR+2HBr$$

$$C_6H_4<\begin{array}{l}CH_2Br\\CH_2Br\end{array}+NHRR' = C_6H_4<\begin{array}{l}CH_2\\CH_2\end{array}>\underset{Br}{N}<\begin{array}{l}R\\R'\end{array}+HBr.$$

Tertiary aliphatic amines give addition products of one molecule of xylylenebromide with two of amine. Tertiary aromatic amines and amino- compounds do not react (Scholtz, Ber. 1898, 31, 1707).

7. *With aromatic aldehydes.*

Primary and secondary amines form compounds with loss of water:

$$C_6H_5CHO+NH_2R = C_6H_5CHNR+H_2O.$$
$$C_6H_5CHO+2NRR'H = C_6H_5CH(NRR')_2+H_2O.$$

Tertiary amines do not react (Schiff, Annalen, 159, 159).

8. *With chloroform and potash.*

Primary amines give isocyanides on warming,

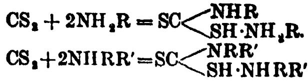
$$RNH_2+CHCl_3+3KOH = RNC+3KCl+3H_2O$$

(Hofmann, Ber. 3, 767).

Secondary and tertiary amines give no characteristic reaction.

9. *With carbon disulphide.*

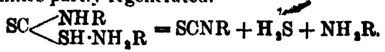
Aliphatic primary and secondary amines react as follows:—



$$CS_2+2NH_2R = SC<\begin{array}{l}NHR\\SH\cdot NH_2R.\end{array}$$

$$CS_2+2NHRR' = SC<\begin{array}{l}NRR'\\SH\cdot NHRR'.\end{array}$$

On boiling the product of the action of CS_2 on primary amines with metallic salts ($HgCl_2$ or $FeCl_3$), mustard oils are produced, and primary amines partly regenerated.



$$SC<\begin{array}{l}NHR\\SH\cdot NH_2R\end{array} = SCNR+H_2S+NH_2R.$$

(Hofmann, Ber. 8, 105, 461; 14, 2754; 15, 1290).

Aromatic amines give substituted thioureas.

$$2RNH_2+CS_2=H_2S+(RNH)_2CS.$$

10. *With the alkali metals.*

Primary and secondary amines dissolve with evolution of hydrogen and formation of substances of the type RNHK or RNK_2. Tertiary amines do not react.

11. *With oxidising agents.*

Oxidation with potassium permanganate decomposes aliphatic amines with formation of aldehydes and acids.

With Caro's acid (H_2SO_5), primary amines of the type RCH_2NH_2 are oxidised to hydroxylamines and hydroxamic acids, all of which give a characteristic colouration with ferric chloride. Ketoximes are formed from amines of the type $RR'CH\cdot NH_2$, whilst those of the type $RR'R''C\cdot NH_2$ give nitroso- and nitro- derivatives (Bamberger, Ber. 1902, 35, 4293; 1903, 36, 710).

With hydrogen peroxide aliphatic, secondary, and tertiary amines give hydroxylamines and N-oxides of type RR'NOH and RR'R''NO (Dunstan and Goulding, Chem. Soc. Trans. 75, 1104).

Oxidation of aniline and its para compounds gives quinone.

12. *With hypochlorous acid.*

Tertiary amines react with hypochlorous acid to give a dialkylchloramine (Meisenheimer, Ber. 1913, 51, 166):

$$(CH_3)_3N+2HClO = (CH_3)_2N\cdot Cl+CH_2O+H_2O+HCl$$

DIAMINES.

These may be regarded as derived from hydrocarbons by replacement of two hydrogen atoms by two amino- groups, or from two molecules of ammonia by replacement of two hydrogen atoms one from each molecule by a hydrocarbon residue. Certain of them occur as decomposition products of the animal organism, the chief of these being *putrescine* (tetramethylene diamine), and *cadaverine* (pentamethylene diamine). Diamino- acids are an important product of the decomposition of proteins.

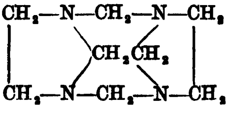
Preparation.—The methods are entirely analogous to those used in the preparation of monamines. Aliphatic diamines are obtained by the action of aqueous ammonia on dihalogen derivatives of hydrocarbons; this method is not generally applicable to the preparation of aromatic mono- or diamino- compounds, but a modification of it, which consists in treatment of *p*-chlormonamines with aqueous ammonia in presence of copper salts, is used in the commercial manufacture of *p*-phenylene diamine and its homologues (Ger. Pat. 204848, 1908). Aromatic diamino- compounds are prepared on the commercial scale chiefly by the reduction of dinitro- compounds; but practically all the methods for the production of monamines are also available for that of diamines.

Properties.—The aliphatic diamines are strongly basic substances, their basicity increasing with the number of methylene groups (Bredig, Zeitsch. physical. Chem. 1894, 13, 308). Their boiling-points are much higher than those of the corresponding monamines. Their hydroxides, which are diacid bases, are extremely stable, and are only decomposed on boiling with caustic alkalis or distillation over metallic sodium. The list of the chief aliphatic diamines and their physical constants (*see* p. 133) is taken from Meyer and Jacobsen's Lehrbuch der Organischen Chemie. The unsubstituted aromatic diamino compounds differ from the corresponding monamines by being easily soluble in water. Their solutions in water are easily oxidised, but the dry bases are stable in air.

Reactions.—Diamines give the ordinary reactions characteristic of the amino- group, but primary aromatic *o*-amino- compounds and to some extent aliphatic diamines, possess in addition, the property of forming condensation products containing nitrogen rings. *m*- and *p*-diamines do not exhibit this property.

1. *With aldehydes.*

With aliphatic diamines, cyclic compounds are formed as well as the ordinary alkylidene bases. Thus the action of formaldehyde on cold solutions of ethylene diamine results in the formation of a compound $C_8H_{18}N_4$, to which the formula

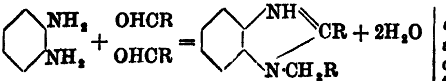


has been assigned (Bischoff, Ber. 1898, 31, 3254).

Aromatic *o*-diamino- compounds give aldehydines or anhydro bases:

ALIPHATIC DIAMINES.

	Formula	M.pt.	B.pt.	Sp.gr.
Ethylenediamine . . .	$NH_2\cdot CH_2\cdot CH_2\cdot NH_2$	+8·5°	116·5°	0·902 (15°)
Propylene „ . . .	$CH_3\cdot CH(NH_2)CH_2\cdot NH_2$	—	119°–120°	0·878 (15°)
Trimethylenediamine . .	$NH_2\cdot CH_2\cdot CH_2\ CH_2\cdot NH_2$	—	135°–136° (738 mm.)	—
αβ-diaminobutane . . .	$CH_3\cdot CH_2\ CH(NH_2)\ CH_2\cdot NH_2$	—	130°–155°	—
αγ- „ „ . . .	$CH_3\cdot CH\cdot(NH_2)\ CH_2\cdot CH_2\cdot NH_2$	—	141° (738 mm.)	—
αδ- „ „ . . .	$NH_2\cdot CH_2\cdot CH_2\ CH_2\ CH_2\cdot NH_2$	27°–28°	158°–160°	—
βγ- „ „ . . .	$CH_3CH(NH_2)\ CH(NH_2)\cdot CH_3$	only known	as its salts	—
αε- „ pentane . .	$NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\ CH_2\ NH_2$	—	178°–179°	0·917 (0°)
βδ- „ „ . .	$CH_3CH(NH_2)\cdot CH_2\cdot CH(NH_2)\ CH_3$	α modification	46°–47° (20 mm.)	—
		β modification	43°–44° (11–12 mm.)	—
β-methyl-αδ-diaminobutane .	$NH_2\cdot CH_2\cdot CH(CH_3)\ CH_2\cdot CH_2\cdot NH_2$	inactive form	172°–173°	0·8836 $\left(\frac{20°}{4°}\right)$
		active form	170°	—
αζ-diaminohexane . . .	$NH_2\cdot CH_2(CH_2)_4CH_2\cdot NH_2$	39°–40°	100° (20 mm.)	—
βε- „ „ . . .	$CH_3\cdot CH(NH_2)(CH_2)_2CH(NH_2)CH_3$	φ derivative	175·5° (753 mm.)	—
		χ „	174·5°-175·5° (752 mm.)	—
β-methyl-αδ-diaminopentane .	$NH_2\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot CH(NH_2)CH_3$	—	175°	—
β-methyl-αε- „ „ .	$NH_2\cdot CH_2\cdot CH\cdot(CH_3)(CH_2)_2CH_2\cdot NH_2$	—	78°–80° (13 mm.)	—
βγ-dimethyl-βγ-diaminobutane	$(CH_3)_2C(NH_2)\cdot C(NH_2)(CH_3)_2$	97°–99°	147°–149° (740 mm.)	—
αη-diaminoheptane . . .	$NH_2(CH_2)_7NH_2$	28°–29°	223°–225°	—
αθ-diaminooctane . . .	$NH_2(CH_2)_8NH_2$	52°	225°–226°	—
βε-dimethyl-βε-diaminohexane .	$(CH_3)_2C(NH_2)(CH_2)_2(NH_2)C(CH_3)_2$	solidifies at 0°	186° (758 mm.)	0·858 $\left(\frac{0°}{0°}\right)$
γδ-dimethyl-γδ-diaminohexane	$C_2H_5\cdot C(CH_3)(NH_2)(NH_2)C(CH_3)\cdot C_2H_5$	only known	as its salts	—
αι-diaminononane . .	$NH_2(CH_2)_9NH_2$	37°–37·5°	258°–259°	—
βζ-dimethyl-βζ-diaminoheptane	$(CH_3)_2C(NH_2)(CH_2)_3(NH_2)C(CH_3)_2$	—	204°–206° (749 mm.)	0·8554 $\left(\frac{0°}{0°}\right)$
ακ-diaminodecane . . .	$NH_2(CH_2)_{10}NH_2$	61·5°	140° (12 mm.)	—
βη-dimethyl-βη-diaminooctane	$(CH_3)_2C(NH_2)(CH_2)_4(NH_2)C(CH_3)_2$	31°	226°–229°	0·8344 $\left(\frac{28°}{0°}\right)$



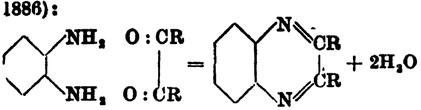
(Ladenburg and Engelbrecht, Ber. 1878, 11, 1653; Hinsberg, *ibid.* 1886, 19, 2025).

The aldehydines are strongly basic bodies, and not decomposed on boiling with dilute acids and alkalis. They are very stable towards oxidising and reducing agents. Their derivatives are used as dyes.

p- and *m*-diamines give alkylidene bases.

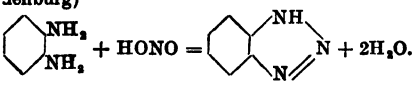
2. *With 1.2-dicarbonyl compounds* (*aldehydes or ketones*).

o-Diamino compounds react to give quinoxaline (azine) derivatives (Hinsberg, Annalen, 342, 1886):



3. *With nitrous acid.*

o-Diamino- compounds form azimines (Ladenburg)



Diamino- compounds both *m*- and *p*- will react in the ordinary way in presence of much hydrochloric acid, giving bis-diazo- compounds; in neutral solutions *m*-diamino- compounds give triamino azo benzene and its homologues. The reaction in the case of *m*-phenylene diamine is:

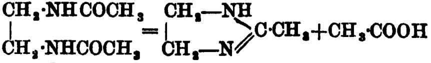
$$2C_6H_4(NH_2)_2 + HONO$$
$$= NH_2{\cdot}C_6H_4{\cdot}N:N{\cdot}C_6H_3(NH_2)_2.$$

The substances formed are brown and very deeply coloured. The reaction is used as a test for the presence of nitrites in water analysis (Griess, Ber. 1878, 11, 624).

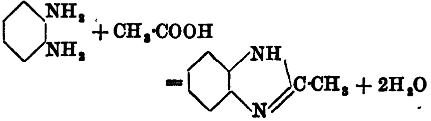
Aliphatic diamines give glycols and oxides

4. *With organic acids, acid chlorides or anhydrides.*

Aliphatic diamines and *m*- and *p*-diamino- compounds form normal derivatives; in the cases of aliphatic substances, these derivatives are partially decomposed on heating, giving cyclic compounds of the iminoazole type:

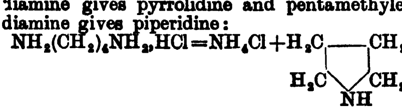


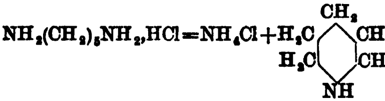
o-Diamino- compounds give similar compounds, without the intermediate formation of the acyl derivative:



5. *With mineral acids.*

All diamines form stable salts. Those of the aliphatic series are decomposed on heating with separation of ammonium salt and formation of cyclic compounds. Thus, tetramethylene diamine gives pyrrolidine and pentamethylene diamine gives piperidine:





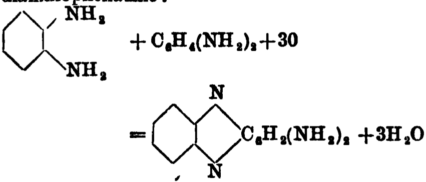
The higher homologues, however, do not form ring compounds containing a corresponding number of atoms in the ring. Thus, octomethylene diamine hydrochloride, on heating, does not give octomethylene imine, which would contain a ring of nine atoms, but 2-butylpyrrolidine. Similarly, decamethylene diamine gives 2-hexylpyrrolidine (Blaise and Houillon, Compt. rend. 1906, 142, 1541; 1906, 143, 361).

The aromatic diamines are the starting-points for the preparation of a large number of dyes, and hence are of commercial importance. The following are the chief members of the series:—

o-Phenylenediamine $C_6H_4(NH_2)_2$. First obtained by Griess by the distillation of *o-m*- and *m-p*- diaminobenzoic acid:

$$\underset{(1,\,2,\,3,\text{ or }1,\,3,\,4)}{C_6H_3(COOH)(NH_2)_2} = \underset{(1,\,2)}{C_6H_4(NH_2)_2} + CO_2$$

(J. pr. Chem. [2] 3, 143). By the reduction of *o*-nitraniline $C_2H_4(NO_2)$ (NH_2) (1, 2) (Zincke and Sintenis, Ber. 6, 123), or of *o*-dinitrobenzene $C_6H_4(NO_2)_2$ (1, 2) (Rinne and Zincke, Ber. 7, 1374), with tin and hydrochloric acid.—Crystallises from water in laminæ, melting at 102°. Boils at 252°. Readily soluble in water, alcohol, and ether. Diacid base, the sulphate $2[C_6H_4(NH_2)_2,H_2SO_4]\ 3H_2O$ forms nacreous laminæ. It gives all the reactions for *o*-diamino-compounds referred to above. On oxidation with ferric chloride it gives a red compound, diaminophenazine:



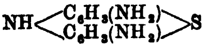
m-Phenylenediamine $C_6H_4(NH_2)_2$. By reducing *m*-dinitrobenzene or *m*-nitraniline with iron filings and acetic acid (Hofmann, Proc. Roy. Soc. 11, 518; 12, 639), or with tin and hydrochloric acid (Gerdemann, Zeitsch. f. Chem. 1865, 61). By reducing either (1, 2, 4)- or (1, 2, 6)-dinitrobenzoic acid with tin and hydrochloric acid, the carboxyl group being eliminated in the process (Zincke and Sintenis, Ber. 5, 791; Griess, Ber. 7, 1223). On a manufacturing scale it is prepared by reducing dinitrobenzene with iron turnings and hydrochloric acid.—Separates from its solutions as an oil which does not readily solidify unless brought in contact with a crystal of the base. Melts at 63°, and boils at 287°. Readily soluble in water. It gives the typical reactions of *m*-diamino- compounds (*see* above).

By the action of a diazobenzene salt on *m*-phenylenediamine, *chrysoïdine* (unsymmetrical diamidoazobenzene) is produced:

$$C_6H_5N_2Cl + C_6H_4(NH_2)_2$$
$$= HCl + C_6H_5N:N{\cdot}C_6H_3(NH_2)_2.$$

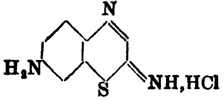
In the manufacture of phenylene-brown and chrysoïdine the solution of crude *m*-phenylenediamine hydrochloride obtained by the reduction of *m*-dinitrobenzene is employed, without first isolating the base. A violet colouring matter is obtained by heating *m*-phenylenediamine with aniline hydrochloride to 190°–200°, and a blue colouring matter by heating it with *m*-phenylenediamine hydrochloride (Krause, Ber. 9, 835).

p-Phenylenediamine $C_6H_4(NH_2)_2$. Obtained by reducing *p*-dinitrobenzene (Rinne and Zincke, Ber. 7, 871), or *p*-nitraniline (Hofmann, Proc. Roy. Soc. 12, 639), or aminoazobenzene (Martius and Griess, J. pr. Chem. 97, 263), with tin and hydrochloric acid, aniline being formed simultaneously in the case of aminoazobenzene. Along with diaminodiphenylamine by reducing aniline-black with tin and hydrochloric acid or with hydriodic acid and amorphous phosphorus (Nietzki, Ber. 11, 1097). By distilling (1, 2, 5)-diaminobenzoic acid (Griess, Ber. 5, 200). By action of *p*-chloraniline on aqueous ammonia in presence of copper salts. Crystals, melting at 147°. Boils at 267°. Sublimes in leaflets. Readily soluble in water, alcohol, and ether. Yields quinone on oxidation. When oxidised in the presence of primary amines or phenols it gives indamines and indophenols, these on heating produce safranines. By heating it with sulphur to 150°–180°, it is converted into diaminothiodiphenylamine (*leucothionine, Lauth's white*)



$$NH\begin{cases}C_6H_3(NH_2)\\C_6H_3(NH_2)\end{cases}S$$

which, when oxidised with ferric chloride, yields thionine (*Lauth's violet*)



The latter colouring matter may also be obtained by the simultaneous oxidation of *p*-phenylenediamine and sulphuretted hydrogen by ferric chloride in aqueous solution (Lauth, Compt. rend. 82, 1441; Bull. Soc. Chim. 25, 422; Bernthsen, Annalen, 230, 108). If dimethyl-*p*-phenylenediamine $C_6H_4(NMe_2)(NH_2)$ is substituted for *p*-phenylenediamine in the foregoing reaction, tetramethylthionine (*methylene blue*) is formed (*v.* Methylene blue).

Tolylene-diamines (*Diaminotoluenes*)

$C_6H_3(CH_3)(NH_2)_2$.

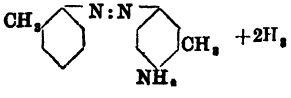
All the six possible compounds are known. Their physical constants are as follows:—

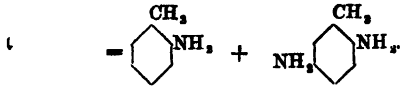
	M.pt.	B.pt.
1-Methyl-2 : 3-diaminobenzene	61°	255°
„ 2 : 4 „ „	99°	283°–285°
„ 2 : 5 „ „	64°	273°
„ 2 : 6 „ „	103°	—
„ 3 : 4 „ „	88°	265°
„ 3 : 5 „ „	—	284°

Only two of these, however, are of technical importance.

Tolylenediamine $C_6H_3(CH_3)(NH_2)_2$ (1, 2, 4). Obtained by the reduction of the corresponding dinitrotoluene. Sparingly soluble in cold, readily soluble in boiling water, in alcohol, and in ether. Forms crystalline salts. As the two amino groups in this compound are in the meta- position to one another, it is an analogue of *m*-phenylenediamine, which it resembles in many of its reactions: thus 2 : 4-tolylenediamine may either wholly or in part replace the *m*-phenylenediamine used in the manufacture of phenylene-brown, producing colouring matters the shade of which is redder than that of ordinary phenylene-brown.

Tolylenediamine $C_6H_3(CH_3)(NH_2)_2$ (1, 2, 5) is obtained by the reduction of the corresponding *m*-nitro-*o*-toluidine $C_6H_3(CH_3)(NH_2)(NO_2)$ (1,2,5) with tin and hydrochloric acid (Beilstein and Kuhlberg, Annalen, 158, 350; Ladenburg, Ber. 11, 1651). Formed along with *o*-toluidine when the aminoazotoluene prepared from *o*-toluidine is treated with the same reducing agent:





The two bases may be separated by fractional distillation (Nietzki, Ber. 10, 832). This reaction is utilised in preparing the mixture of *o*-toluidine and γ-tolylene-diamine which, after the addition of a second molecule of a monamine (either aniline or *o*- or *p*-toluidine), yields on oxidation safranine. On a large scale the aminoazotoluene is reduced with iron turnings and hydrochloric acid. Crystallises in colourless rosettes of tabular crystals. Readily soluble in water, alcohol, and ether, sparingly soluble in benzene. Yields on oxidation toluquinone $C_6H_3(CH_3)O_2$.

Other diamines of this series are—

Xylylene diamines:

1.3-dimethyl, 2.4-diaminobenzene, m.p. 64°.
1.3- „ 4.6 „ „ „ 104°.
1.3- „ 2.5 „ „ „ 77°.

Diaminotrimethylbenzenes: diamino-pseudocumenes:

1.2.4-trimethyl, 5.6-diaminobenzene, m.p. 90°.
1.2.4- „ 3 6 „ „ m.p. 78°.

Diamino mesitylene:

1.3.5-trimethyl, 2.4-diaminobenzene, m.p. 90°.

Similar diamines have been prepared from naphthalene and other hydrocarbons.

TRIAMINES, TETRAMINES, AND PENTAMINES.

Very few of these substances are known. Their properties are similar to those of other substances containing the amino group.

1.2.3-*triaminopropane*; b.p. 190° (Curtius, J. pr. Chem. 1900, 62, 232).

2.3.5-*triaminohexane* (Morelli and Marchetti, Atti del Accad. Lin. 1908, [5] 17, 1, 250).

The three modifications of triaminobenzene are all known.

1.2.3-*triaminobenzene*; m.p. 103°; b.p. 336°.

1.2.4-*triaminobenzene* is formed by reduction of *o*-*p*-dinitraniline or of chrysoidine. On oxidation it gives triaminophenazin.

1.3.5-*triaminobenzene* is only known in the form of its salts.

1.2.3.4. and 1.2.4.5-*tetraminobenzenes* prepared by the reduction of oximes and nitro compounds, have been isolated as their sparingly soluble sulphates (Nietzki and Schmidt, Ber. 1889, 22, 1648; Nietzki, Ber. 1887, 20, 2114).

Pentaminobenzene has been obtained as the hydrochloride with 3 molecules of HCl, by reduction of triaminodinitrobenzene (from tribrombenzene and ammonia). Pentaminotoluene has been similarly obtained.

Reduction of triaminotrinitrobenzene gives pentaminobenzene (Palmer and Jackson, Ber. 1888, 21, 1706; Palmer and Grindley, *ibid.* 1893, 26, 2304). T. S. M.

AMINO-ACIDS. The amino-acids may be conveniently described under the two headings (*a*) *Aliphatic Amino-acids*, and (*b*) *Aromatic Amino-acids.*

Aliphatic Amino-acids. The amino-fatty acids are of great physiological importance, many of them occurring in plant and animal organisms. They are products of proteid degradation, and may be obtained from proteins by heating with hydrochloric acid or baryta water. The general methods in use for preparing these acids are:

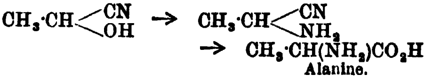
(i.) By treating the monohalogenated fatty acids with ammonia:

$CH_2Cl{\cdot}COOH \rightarrow CH_2(NH_2)COOH$

Chloracetic acid. Glycine.

For examples, *cf.* Fischer and Smits (Ber. 1906, 39, 351).

(ii.) By heating the cyanhydrin of an aldehyde or ketone with ammonia and then hydrolysing the product, whereby an *α*-amino-acid is produced:



$$CH_3{\cdot}CH\genfrac{<}{}{0pt}{}{CN}{OH} \rightarrow CH_3{\cdot}CH\genfrac{<}{}{0pt}{}{CN}{NH_2} \rightarrow CH_3{\cdot}CH(NH_2)CO_2H$$

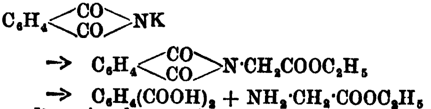
Alanine.

(iii.) By the reduction of the cyanofatty acids with nascent hydrogen (Zn or HCl or by heating with HI):

$$CN{\cdot}CO{\cdot}OH + 2H_2 = CH_2(NH_2)CO_2H$$

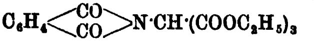
Cyanoformic acid.

(iv.) By Gabriel's phthalimide reaction (*v.* preparation of amines 4 (*b*)), using a halogen substituted ester instead of an alkyl haloid:



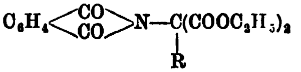
$$C_6H_4\genfrac{<}{>}{0pt}{}{CO}{CO}NK \rightarrow C_6H_4\genfrac{<}{>}{0pt}{}{CO}{CO}N{\cdot}CH_2COOC_2H_5 \rightarrow C_6H_4(COOH)_2 + NH_2{\cdot}CH_2{\cdot}COOC_2H_5$$

By using brommalonic ester the compound



$$C_6H_4\genfrac{<}{>}{0pt}{}{CO}{CO}N{\cdot}CH{\cdot}(COOC_2H_5)_3$$

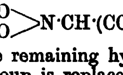
is obtained. The remaining hydrogen atom of the methylene group is replaceable by sodium, and by reacting with alkyl haloids on the sodium compound, compounds of the general formula



$$C_6H_4\genfrac{<}{>}{0pt}{}{CO}{CO}N{-}\underset{\displaystyle R}{\underset{|}{C}}(COOC_2H_5)_2$$

are obtained. From these, by suitable treatment, it is easy to get acids of the general formula $NH_2{\cdot}CHR{\cdot}COOH$ (Sörenson, Zentralblatt. 1903, ii. 33).

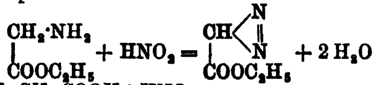
The amino-acids are crystalline bodies with high melting-points, usually soluble in water, but sparingly soluble in alcohol and ether. The *α*- compounds are sweet, the *β*-compounds less so, and the *γ*-compounds not at all. Moulds grow well in solutions of *γ*-amino-acids, less well in *β*-acids, and hardly at all in *α*-acids. They are amphoteric, *i.e.* feeble bases and feeble acids, and there is reason to think that in solution they exist as internal salts, *e.g.* glycocoll:



$$\begin{array}{l}CH_2{-}NH_3\\ \qquad\quad |\\ CO{-}O.\end{array}$$

They have, in addition to the properties characteristic of amines and of acids, the following special properties:—

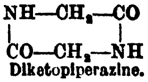
(1) Their esters, with nitrous acid, give diazo- compounds, although the acids themselves undergo with nitrous acid the normal reaction of aliphatic amines



$$\begin{array}{l}CH_2{\cdot}NH_2\\ |\\ COOC_2H_5\end{array} + HNO_2 = \begin{array}{l}CH\genfrac{<}{}{0pt}{}{N}{N}\!\!\Vert\\ |\\ COOC_2H_5\end{array} + 2\,H_2O$$

$$NH_2{\cdot}CH_2{\cdot}COOH+HNO_2 = HO{\cdot}CH_2{\cdot}COOH+H_2O$$

(2) Anhydrides, which are in fact derivatives of piperazine, are formed by *α* amino-acids, *e.g.* glycocoll gives glycide



$$\begin{array}{l}NH{-}CH_2{-}CO\\ |\qquad\qquad\ \ |\\ CO{-}CH_2{-}NH\end{array}$$

Diketopiperazine.

Heating with glycerol promotes the formation of these anhydrides (L. C. Maillard, Ann. Chim. 1915 [ix.] 3, 48; 4, 225).

Important amino-acids are glycine, alanine, phenylalanine, tyrosine, leucine, valine, serine, cystine, tryptophane, histidine, arginine, lysine, aspartic acid, and glutaminic acid, which are described under their respective headings (*v.* also PROTEINS).

(*b*) **Aromatic Amino-acids.** A true aromatic amino-acid such as anthranilic acid, contains both the amino- and the carboxyl- groups united to carbon atoms in the benzene ring. Isomeric with these are acids which contain the amino-group or the carboxyl- group or both, introduced into fatty side chains, the last two classes being really substituted fatty acids.

The general methods in use for preparing aromatic amino-acids are:

(i.) By reducing the corresponding nitro-acids:

$C_6H_4(NO_2)COOH(1{:}2) \rightarrow C_6H_4(NH_2)COOH(1{:}2)$

o-nitrobenzoic acid. Anthranilic acid.

(ii.) By treating the halogen substituted esters of carboxylic acids with potassium phthalimide and hydrolysing the product with hydrochloric acid at 200°.

The aromatic amino-acids are used in the preparation of azo-dyestuffs (*q.v.*).

o-Aminobenzoic acid. Anthranilic acid

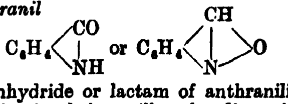
$$C_6H_4(NH_2)CO_2H \quad (1:2)$$

It was first obtained by heating indigo with caustic potash (Fritzsche, Annalen, 39, 83). It may be prepared by the reduction of *o*-nitrobenzoic acid with tin and hydrochloric acid (Beilstein and Kühlberg, Annalen, 163, 138), or with zinc and sodium bisulphite (Goldberger, Chem. Zentr. 1900, ii. 1014; *v.* also Preuss and Binz, Zeitsch. angew. Chem. 1900, [16] 385 and Bad. Anil. u. Soda Fab. Eng. Pat. 18319; J. Soc. Chem. Ind. 1900, 774); by heating *o*-chlorbenzoic acid and ammonia at 125° under pressure (Farbw. Meister, Lucius und Brüning, D. R. P. 145604; Chem. Soc. Abst. 1904, i. 50); by treating phthalimide with sodium hypochlorite and hydrochloric acid or bromine and caustic potash (Hoogewerff and van Dorp, Ber. 1891, Ref. 966; Bad. Anil. und Soda Fab. D. R. P. 55988; Frdl. ii. 546; Amsterdamsche Chininefabrik, Eng. Pat. 18246; J. Soc. Chem. Ind. 1891, 831); by boiling phthalhydroxylamic acid, formed by treating phthalic anhydride with hydroxylamine, with caustic soda or sodium carbonate (Cie. Par. de Coul. d'Aniline, Fr. Pat. 318050; J. Soc. Chem. Ind. 1902, 1392; Farbw. Meister, Lucius und Brüning, Eng. Pat. 1982, D. R. P. 136788; Basler Chemische Farbw.; D. R. PP. 130301, 130302); by reducing sulphanthranilic acid electrolytically or with sodium amalgam (Kalle and Co. D. R. P. 129165; Chem. Zentr. 1902, i. 1138; D. R. P. 146716; Chem. Soc. Abst. 1904, i. 159); by treating *o*-nitrotoluene with concentrated alcoholic or aqueous alkali (Bad. Anil. und. Soda Fab. D. R. P. 114839; Chem. Zentr. 1900, ii. 1892); by heating isatoic acid with concentrated hydrochloric acid (Kolbe, J. pr. Chem. [2] 30, 124); and by oxidising aceto-*o*-toluidide with permanganate in presence of magnesium sulphate and hydrolysing the product (Bad. Anil. und Soda Fab. D. R. P. 94629).

Anthranilic acid is of great commercial importance, as it is one of the intermediate products in the manufacture of synthetical indigo. It crystallises in colourless plates, m.p. 144·6°, and is readily soluble in alcohol or water. It condenses with formaldehyde, forming compounds which are of use in the preparation of indigo (Heller and Fiesselmann, Annalen, 324, 118; Bad. Anil. und Soda Fab. D. R. PP. 117924, 158090, 158346; J. Soc. Chem. Ind. 1905, 615). Reduction with sodium amalgam in hydrochloric acid solution yields *o*-aminobenzylalcohol (Langguth, Ber. 1905, 2062). Concentrated hydriodic acid decomposes it at 200° into ammonia, carbon dioxide, aniline and benzoic acid (Kwisda, Monatsh. 12, 427); whilst nitrous acid converts it in aqueous solution into salicylic acid. Anthranilic acid is employed in the preparation of azo- dyestuffs (*q.v.*) (*v.* also Bayer and Co. D. R. P.P 58271, 60494, 60500, 86314; Frdl. iii. 614 *et seq.*; iv. 795).

The methyl ester of anthranilic acid occurs in Neroli oil (oil of orange flowers) (Walbaüm, J. pr. Chem. 1899, 59, [6–7] 350). It is prepared by heating anthranilic acid with methyl alcohol and hydrochloric acid (Erdmann, Ber. 1899, 1213; D. R. P. 110386) or from acetylanthranilic acid, methyl alcohol and mineral acids (Erdmann, D. R. P. 113942; Chem. Zentr. 1900, ii. 831). It is a crystalline solid, m.p. 24·5°, b.p. 135·5° (15 mm.). The ethyl ester melts at 13° and boils at 136°–137° (13·5 mm.); at 266°–268° (corr.) (Frankel and Spiro, Ber. 1895, 1684) Aminobenzoic acid alkamine esters (*v. p*-aminobenzoic acid).

Anthranil



is the anhydride or lactam of anthranilic acid, its constitution being still under discussion. It is prepared by treating the dimercury derivative of *o*-nitrotoluene (obtained by suspending *o*-nitrotoluene in water and heating it with freshly precipitated mercuric oxide and caustic soda) with concentrated hydrochloric acid and decomposing the product with water (Kalle and Co. Fr. Pat. 370522; D. R. P. 194364; J. Soc. Chem. Ind. 1907, 278; 1908, 713); by heating *o*-nitrotoluene with caustic soda to 170° (Kalle and Co. D. R. P. 194811; Chem. Soc. Abstr. 1908, i. 786); by the reduction of *o*-nitrobenzaldehyde with aluminium amalgam (Brühl, Ber. 1903, 3634); and by the oxidation of *o*-aminobenzaldehyde with a neutral solution of Caro's persulphuric acid (Bamberger and Demuth, Ber. 1903, 829; 2042).

Anthranil is an oil, readily volatile in steam, possesses a peculiar odour, and boils at 210°–213°. It dissolves in alkalis to form salts of anthranilic acid and on treatment with acetic anhydride yields acetylanthranilic acid.

***m*-Aminobenzoic acid.** *Benzamic acid* $C_6H_4(NH_2)CO_2H$ (1 : 3), is prepared by reducing *m*-nitrobenzoic acid with ammonium sulphide and subsequently precipitating the acid with tartaric acid (Holleman, Rec. Trav. Chim. 1902, [ii.] 21, 56; *v.* also Gerland, Annalen, 91, 188). It is a colourless crystalline solid, m.p. 174°; sparingly soluble in cold, readily so in hot water. Reduction with sodium amalgam in hydrochloric acid yields *m*-aminobenzyl alcohol (Langguth, Ber. 1905, 2062). Concentrated hydriodic acid transforms it into ammonia and benzoic acid (Kwisda, Monatsh. 12, 428). *m*-Aminobenzoic acid is used in the preparation of azo-dyestuffs (*q.v.*) (Bayer and Co., D. R. PP. 58271, 59081, 60494, 60500, 63104, 64529, 69445, 74198, 74516, 78493, 86314; Frdl. iii. 614 *et seq.*, 777 *et seq.*; iv. 793, 795; Ges. f. Chem. Ind., D. R. P. 76127; Frdl. iii. 746). Aminobenzoic acid alkamine esters (*v. p*-aminobenzoic acid).

p-Aminobenzoic acid $C_6H_4(NH_2)CO_2H$ (1 : 4), is prepared by the reduction of *p*-nitrobenzoic acid with ammonium sulphide (Fischer, Annalen, 127, 142) or with tin and hydrochloric acid (Beilstein and Wilbrand, Annalen, 128, 164). It is a colourless crystalline solid, m.p. 186°–187°, readily soluble in water, alcohol, or ether. Strong hydrochloric acid at 180° converts it into aniline and carbon dioxide (Weith, Ber. 1879, 105) and hydriodic acid at 200° into ammonia, carbon dioxide, and benzoic acid (Kwisda, Monatsh. 12, 428). *p*-Aminobenzoic acid is used in the preparation of azo- dyestuffs (*q.v.*) (Bayer and Co. D. R. PP. 58271, 60494, 60500, 86314; Frdl. iii. 614 *et seq.*; iv. 795; Ges. f. Chem. Ind., D. R. P. 76127; Frdl. iii. 746).

Many complicated alkyl- and alkamine esters of the aminobenzoic acids have been prepared and they are claimed to be valuable anæsthetics (Farbw. Meister, Lucius, and Bruning, D. R. PP. 170587, 172301, 172447, 172568, 179627, 180291, 180292, 194748, Eng. Pat. 17162, Fr. Pat. 361734, U. S. Pat. 812554; J. Soc. Chem. Ind. 1906, 607; 1907, 434; Chem. Soc. Abstr. 1906, i. 845 *et seq.*; 1907, i. 923; 1908, i. 638; Merck, D. R. P. 189335; J. Soc. Chem. Ind., 1908, 471; Bayer and Co. D. R. PP. 211801, 218389, Eng. Pat. 4321; J. Soc. Chem. Ind. 1909, 854; Chem. Zentr. 1910, i. 782; Fritzsche, Eng. Pat. 2020, Fr. Pat. 398259, D. R. P. 213459; J. Soc. Chem. Ind. 1909, 814).

4-*Amino-o-toluic acid* $C_6H_3{\cdot}CH_3(NH_2)CO_2H$ (1 : 4 : 2); m.p. 196°. Obtained by the reduction of 4-nitrotoluic acid with tin and hydrochloric acid (Jacobsen and Wierss, Ber. 1883, 1959).

5-*Amino-o-toluic acid* $C_6H_3{\cdot}CH_3(NH_2)CO_2H$ (1 : 5 : 2); m.p. 153°, is obtained by the reduction of 5-nitrotoluic acid with tin and hydrochloric acid (Jacobsen, Ber. 1884, 164).

6-*Amino-o-toluic acid* $C_6H_3{\cdot}CH_3(NH_2)CO_2H$ (1 : 6 : 2). Method of preparation as above; m.p. 191° (J. and W. *l.c.*).

2-*Amino-m-toluic acid* $C_6H_3{\cdot}CH_3(NH_2)CO_2H$ (1 : 2 : 3). Method of preparation as above; m.p. 132° (Jacobsen, Ber. 1881, 2354), 172° (Jürgens, Ber. 1907 4409).

4-*Amino-m-toluic acid* (*Methylanthranilic acid*) $C_6H_3{\cdot}CH_3(NH_2){\cdot}CO_2H$ (1 : 4 : 3). Obtained by reduction of 4-nitro-*m*-toluic acid with tin and hydrochloric acid (Jacobsen, Ber. 1881, 2354) or by treating *p*-methylisatoic acid with concentrated hydrochloric acid (Panaotovic, J. pr. Chem. [2] 33, 62); m.p. 172° (Ehrlich, Ber. 1901, 3366), 175° (Findeklee, Ber. 1905, 3533).

6-*Amino-m-toluic acid* $C_6H_3{\cdot}CH_3(NH_2)CO_2H$

(1 : 6 : 3); m.p. 167°. Obtained by reduction of 6-nitro-*m*-toluic acid (Beilstein and Kreusler, Annalen, 144, 147).

2-Amino-p-toluic acid $C_6H_3{\cdot}CH_3{\cdot}(NH_2){\cdot}CO_2H$ (1:2:4); m.p. 164°–165°. Method of preparation as above (Ahrens, Zeitsch. f. Chemie, 1869, 104).

3-Amino-p-toluic acid (*Homo-anthranilic acid*) $C_6H_3{\cdot}CH_3(NH_2)CO_2H$ (1 : 3 : 4); m.p. 177°. Method of preparation as above (Niementowski and Rozanski, Ber. 1888, 1997; Noyes, Amer. Chem. J. 10, 479).

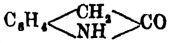
1′-Amino-o-toluic acid (*Benzylamine-o-carboxylic acid*) $NH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$ (1 : 2). Obtained by digesting 1 part of *o*-cyanobenzylphthalimide with 4 parts of concentrated sulphuric acid (Gabriel, Ber. 1887, 2231). Crystalline non-volatile solid.

1′-Amino-m-toluic acid (*Benzylamine-m-carboxylic acid* $NH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$ (1 : 3); m.p. 215°–218°. By heating at 200° a mixture of 2 grams *m*-cyanobenzylphthalimide and 10 c.c. concentrated hydrochloric acid (Reinglass, Ber. 1891, 2419).

1′-Amino-p-toluic acid (*Benzylamine-p-carboxylic acid*) $NH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$ (1 : 4). Method of preparation as above (Günther, Ber. 1890, 1060). Crystalline solid.

2-Amino-α-toluic acid (*2-Aminophenylacetic acid*) $NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ (1 : 2) is not known in the free state; all attempts to prepare it result in the formation of its anhydride, oxindole.

Oxindole



$$C_6H_4{<}\begin{matrix}CH_2\\NH\end{matrix}{>}CO$$

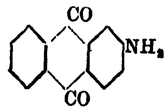
is obtained by treating 2-nitro-α-toluic acid with tin and hydrochloric acid (Bayer, Ber. 1878, 583), or by reducing dioxindole with tin and hydrochloric acid, or with sodium amalgam (Bayer and Knop, Annalen, 140, 29). Crystallises in colourless needles; m.p. 120°.

3-Amino-α-toluic acid (*3-Aminophenylacetic acid*) $NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ (1 : 3). Obtained by reducing 3-nitro-α-toluic acid with tin and hydrochloric acid; m.p. 148°–149° (Gabriel and Borgmann, Ber. 1883, 2065).

4-Amino-α-toluic acid (*4-Aminophenylacetic acid*) $NH_2{\cdot}C_2H_4{\cdot}CH_2{\cdot}CO_2H$ (1 : 4). Method of preparation as above (Radziozewski, Ber. 1869, 209); m.p. 199°–200° (Bedson, Chem. Soc. Trans. 1880, 92).

α-Aminophenylacetic acid $C_6H_5{\cdot}CH(NH_2)CO_2H$. Obtained by heating α-phenylbromacetic acid with aqueous ammonia at 100°–110° (Stückenius, Ber. 1878, 2002); m.p. 256° (Tiemann, Ber. 1880, 383). Sublimes without melting at 265° (Elbers, Annalen, 227, 344). T. S. M.

2-AMINOANTHRAQUINONE



red needles; m.p. 302°. Is employed in the manufacture of indanthrene and indanthrene dyes (*v.* INDANTHRENE). It is made technically by heating under pressure at 170°, a mixture of sodium anthraquinone-2-sulphonate with an aqueous solution of barium chloride and dilute ammonia. The filtered product is washed with water, dilute hydrochloric acid, and weak sodium hydroxide solutions, and is crystallised from chlorobenzene (Farbw. vorm Meister, Lucius und Brüning, D. R. P. 267212).

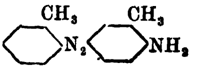
Or the sodium anthraquinone-2-sulphonate, in the form of a paste, is mixed with manganese dioxide and ammonia solution, and heated at 200°. The product is treated with sulphurous acid or acid sodium sulphite to remove the manganese, and dried.

A mixture of sodium dichromate and ammonium chloride may be substituted for the manganese dioxide (Bad. Anilin und Soda Fab. D. R. P. 256515). For details, *see* Cain's Intermediate Products for Dyes.

Alternative methods are to condense *m*-aminobenzoylbenzoic acid by means of sulphuric acid (Basle Chem. Works, D. R. P. 148110), or the carbamide derivative of the same acid (Akt. für Anilinfab. Eng. Pat. 8914, 1914); by hydrolysing 2-*p*-toluenesulphonylaminoanthraquinone (Ullmann, D. R. P. 224982); by the action of ammonia and oxidising agents on *meso*halogen anthracene-2-sulphonic acids (Bad. Anilin und Soda Fab. D. R. P. 288996); or by heating 2-chloroanthraquinone with ammonia (Farbenfab. vorm. F. Bayer and Co. D. R. P. 295624).

AMINOAZOBENZENE (*Aniline yellow*) *v.* AZO- COLOURING MATTER.

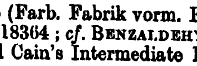
***o*-AMINOAZOTOLUENE**



may be made by heating to 25°–30° *o*-toluidine with an aqueous solution of sodium nitrite and hydrochloric acid in a lead-lined iron pan fitted with a jacket for water-cooling and a stirring arrangement. The excess of toluidine is removed by neutralising with hydrochloric acid when the *o*-aminoazotoluene hydrochloride separates out. It is employed in the manufacture of cloth reds and safranine, and is sold as Yellow Fat colour and as Fast Azo- Garnet base (*cf.* Cain's Intermediate Products for Dyes).

The base is sparingly soluble in water, readily soluble in alcohol and ether; m.p. 100°.

m-**AMINOBENZALDEHYDE** is prepared by heating a mixture of *m*-nitrobenzaldehyde with a solution of sodium hydrogen sulphite and ferrous oxide, made by boiling a solution of ferrous sulphate with chalk. After filtration the solution is acidified and boiled to expel sulphur dioxide (Farbw. vorm. Meister, Lucius und Bruning, D. R. P. 62950, 66241). Or the nitrobenzaldehyde may be heated with an aqueous solution of sodium hyposulphite, the solution cooled, mixed with hydrochloric acid, again boiled to expel sulphur dioxide. On cooling, the anhydro- derivative of *o*-aminobenzaldehyde

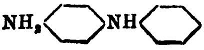


separates out (Farb. Fabrik vorm. F. Bayer und Co. D. R. P. 218364; *cf.* BENZALDEHYDE, *Derivatives* of; and Cain's Intermediate Products for Dyes).

α-**AMINOCAPROIC ACID** *v.* LEUCINE.

p-**AMINOCARVACROL.** A photographic developer, resembling metol and *p*-aminophenol in developing properties; its solution keeps better than that of the latter. Obtained by reducing an ammoniacal solution of *p*-nitroso carvacrol by hydrogen sulphide when *p*-amino carvacrol separates in colourless leaves (Brit. J. Phot. 1910, 56, 534).

***p*-AMINODIPHENYLAMINE**

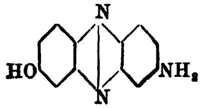


m.p. 75°; b.p. 354° (in hydrogen), is prepared by heating together in an oil-bath at 180°–185° a mixture of sodium 2-chloro-5-nitrobenzenesulphonate (from *p*-chloronitrobenzene), glycerol, chalk, and aniline. After dilution with water, sodium carbonate is added, and the excess of aniline removed by steam distillation. After filtration sodium *p*-nitrodiphenylamine-*o*-sulphonate crystallises out. This is warmed with hydrochloric acid, and nitrodiphenylaminesulphonic acid is formed as a brownish-red oil, which by further heating is converted into the crystalline *p*-nitrodiphenylamine. This is separated, treated with ammonia, washed, and dried. To reduce it, it is dissolved in alcohol, ammonium chloride added, heated to boiling, and mixed with zinc-dust, and a small quantity of a solution of sodium hydrogen sulphite, the whole filtered into 50 p.c. sulphuric acid, when insoluble aminodiphenylamine sulphate separates out. By treating this salt with water and ammonia the free base is obtained. (For details, *see* Cain's Intermediate Products for Dyes.)

AMINOETHYL ALCOHOL *v.* CHOLINE.

4-β-AMINOETHYLGLYOXALINE *v.* ERGOT.

3-AMINO-7-HYDROXYPHENAZINE

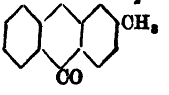


is obtained, according to Nietzki and Simon (Ber. 1895, 28, 2974), by heating an aqueous solution of 2 : 4-diamino-4′-hydroxydiphenylamine hydrochloride with ammonia and manganese oxide until the blue colour disappears, filtering, and acidifying with hydrochloric acid, when the phenazine hydrochloride separates. The free base is obtained by treating the hydrochloride with sodium carbonate.

Ullmann and Gnaedinger (Ber. 1912, 45, 3442) blow air through a solution of *m*-phenylenediamine sulphate and *p*-aminophenol hydrochloride, containing sodium hydroxide. The compound $NH : C_6H_3(NH_2) : N{\cdot}C_6H_4{\cdot}OH,2H_2O$ is obtained, which, on solution in ammonia, warmed, and again treated with air until the blue colour changes to red, yields, after filtration and addition of hydrochloric acid, the phenazine hydrochloride.

3-Amino-7-hydroxyphenazine melts at 360°, and dissolves in alcohol or ether with a green fluorescence.

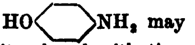
1-AMINO-2-METHYLANTHRAQUINONE



Obtained by adding sodium nitrate to a cooled solution of methylanthraquinone in sulphuric acid and reducing the 1-nitro-2-methylanthraquinone so formed by sodium sulphide or stannous hydroxide; m.p. 202°. Insoluble in water; readily soluble in alcohol, ether, benzene, or acetic acid (Römer and Link, Ber. 1883, 16, 695; Scholl and Holdermann, Ber. 1907, 40, 1696).

AMINONAPHTHOL SULPHONIC ACIDS *v.* NAPHTHALENE.

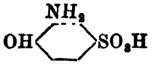
AMINONAPHTHOPHENAZINE *v.* AZINES.

***p*-AMINOPHENOL**  may be made by reducing *p*-nitrophenol with tin and hydrochloric acid in presence of sulphuric acid when *p*-aminophenol sulphate separates. The base is liberated by sodium carbonate, acid sodium sulphite being added to prevent oxidation. The reduction may also be made by sodium hyposulphite in alkaline solution, or by iron, ferrous chloride, and hydrochloric acid, or by the catalytic action of nickel.

p-Aminophenol may also be prepared by reducing *p*-azophenol $OH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}OH$, with stannous chloride or zinc-dust and sodium hydroxide; or by the action of sodium hyposulphite or sodium sulphide on a hot alkaline solution of *p*-hydroxyazobenzene. The *p*-aminophenol sulphate may be obtained from a solution of nitrobenzene in sulphuric acid by the action of zinc-dust, or by electrolytic reduction using carbon cathodes (Darmstadter, D. R. P. 150800); or a copper cathode in a lead cylinder as an anode (Soc. Chem. Ind. Basle, Eng. Pat. 18081, 1915).

p-Aminophenol forms white crystalline plates melting at 184°. It rapidly oxidises in air. Comes into commerce as *Ursol P* for dyeing fur, and as a photographic developer under the name of *Rodinal.*

2-AMINOPHENOL-4-SULPHONIC ACID



Obtained by nitrating phenol-*p*-sulphonic acid with nitric acid and reducing with iron; or by sulphonating *o*-aminophenol; or by fusing aniline-2 : 5-disulphonic acid with sodium hydroxide.

AMINOPHENOPHENANTHRAZINE *v.* AZINES.

AMINOPHENYLACETIC ACID *v.* AMINO-ACIDS (AROMATIC).

α- and β-AMINOPROPIONIC ACIDS *v.* ALANINE.

AMINOSALICYLIC ACID *v.* SALICYLIC ACID.

α-AMINO-*iso*-VALERIC ACID *v.* VALINE.

AMLA (Beng.), **AMLIKA** (Hind.), **AMLIKU** (Ass.), **OWLA** (Mechi), **NELLI** and **TOPPINELLI** (Tam.). A euphorbiaceous Indian tree, *Phyllanthus emblica* (Linn.), the fruits of which (*Emblic myrobalans*) are used in a fresh condition as a laxative, and, when dried, as an astringent (Dymock, Pharm. J. [3] 10, 382). The fruits are also pickled and eaten, and used for tanning and dyeing.

AMMONAL *v.* EXPLOSIVES.

AMMONIA. *Volatile alkali, alkaline air, spirit of hartshorn.* Solutions of ammonia have been known from very early times, but the substance itself was first clearly recognised by

Priestley, who obtained it by heating the aqueous solution and collecting the gas, which he termed *alkaline air*, over mercury. Scheele proved that it contained nitrogen; and Berthollet, and more accurately Austin, demonstrated its real nature, and determined the proportions of its constituents.

Ammonia (or its salts) is found in small quantities in the air, and in most natural water; in the juice of plants, in most animal fluids, in many soils, and in a few minerals, ochres, clays, marls, &c. Ammonia can be obtained synthetically in small quantity by the passage of electrical discharges through a mixture of nitrogen and hydrogen (Donkin, Pogg. Ann. 21, 281); or heating the mixture to a high temperature (Haber, Zeitsch. Elektrochem. 1914, 20, 597; Maxted, Chem. Soc. Trans. 1918, 113, 168, 386; 1919, 115, 113; J. Soc. Chem. Ind. 1918, 37, 232); or as nitrite by the action of a strong induction spark on a mixture of nitrogen and water vapour (Thénard, Compt. rend. 76, 983); or as chloride by sparking a mixture of hydrogen, nitrogen, and hydrogen chloride (Deville, Compt. rend. 60, 317); or by the action of heated spongy platinum, pumice, &c., on a mixture of hydrogen and nitric acid.

For laboratory purposes the gas is usually prepared by heating a mixture of ammonium chloride or sulphate with slaked lime, or by gently warming the concentrated solution, and drying the gas over quicklime. (For the preparation of the chemically pure gas, *see* Stas, Zeitsch. anal. Chem. 6, 423.)

Ammonia is a colourless gas, having a very pungent characteristic smell, and is poisonous when breathed in quantity, destroying the mucous membrane. It has a sp.gr. of 0·5967 (air = 1), 1 litre of the gas at 0° and 760 mm. weighing 0·7708 gram, and readily liquefies on compression, the critical temperature being 132·9°±0·1, and the critical pressure 112·3±0·1 atm. (Cardoso and Gillay, J. chim. phys. 1912, 10, 514). Its critical density is 0·2362 (Berthoud). Liquid ammonia is colourless and very mobile, and has a sp.gr. at 0°/4° of 0·6385 (Dieterici), 0·6388 (Drewes), the coefficient of expansion being very high and increasing rapidly with the temperature. It boils under atmospheric pressure at −33·2-34·6° (Burrell and Robertson), and freezes to a white crystalline solid at −77° (Keyes and Brownlee), −77° (Brill), the vapour pressure being as follows (Regnault, J. 1863, 70):—

at	−30°	1·14 atm.	at	0°	4·19 atm.
„	−20°	1·83 „	„	10°	6·02 „
„	−10°	2·82 „	„	20°	8·41 „

The dependence of the vapour pressure on temperature down to the freezing-point may be expressed by the equation: $\log p = -1969{\cdot}65/T + 16{\cdot}19785 - 0{\cdot}0423858T + 5{\cdot}4131 + 10^{-5}T^2 - 3{\cdot}2715 \times 10^{-8}T^3$.

Its latent heat of evaporation decreases from 333·0 Cal. at −42° to 252·6 Cal. at 49°. The variation of the latent heat with the temperature may be expressed by the formula

$$L = 32{\cdot}968\sqrt{133-\theta} - 0{\cdot}5985(133-\theta)$$

in which θ represents the actual temperature and 133 the critical temperature. The specific heat of saturated ammonia vapour expressed in joules per gram per degree varies from −4·42 at −45° to −3·36 at 45°. To reduce these numbers to 20° Calories, they must be divided by 4·163 (Osborne and van Dusen, J. Amer. Chem. Soc. 1918, 40, 14). The specific heat of liquid ammonia increases from 1·058 at −45° to 1·173 at 45°. Its dependence on temperature may be expressed by the equation:

$$c = 0{\cdot}7498 - 0{\cdot}000136\theta + 4{\cdot}0263\sqrt{133-\theta}$$

in which c is expressed in terms of the 20° Calorie and θ is the temperature (Osborne and van Duser, *l.c.*). Liquid ammonia is produced commercially in large quantity for employment in freezing machines. In many of its physical properties the liquid resembles water, and it acts as a solvent for a large number of substances.

Ammonia gas burns with difficulty in the air when cold, but inflames more readily on heating, and still more readily in oxygen, giving a greenish-yellow flame of high temperature. In presence of suitable catalysts, such as copper, iron, nickel, and especially platinum, ammonia is oxidised by oxygen at lower temperatures with production of oxides of nitrogen, the manufacture of nitric acid from ammonia by Ostwald's process (Eng. Pat. 698, 1902) being carried out in this manner. A number of the elements, when heated in ammonia gas, yield corresponding nitrides: boron, magnesium, and titanium being especially active in this respect, whilst the alkali metals give rise to amides. With carbon at temperatures above 750° ammonia is partly dissociated, and partly converted into hydrocyanic acid, the presence of the latter in crude coal gas being largely due to this reaction.

Many salts combine with ammonia to form stable compounds at the ordinary temperature, the ammonia playing the same part as water of crystallisation. It is evolved on heating, liquid ammonia having been first obtained by Faraday, in 1823, by warming the compound with silver chloride $2AgCl,3NH_3$, in a sealed tube.

The action of heat upon ammonia has been investigated by Ramsay and Young (Chem. Soc. Trans. 45, 92), Perman (Proc. Roy. Soc. 74, 110; 76A, 167), Haber and v. Oordt (Zeitsch. anorg. Chem. 44, 341), and Nernst and Jost (Zeitsch. Elek. 13, 521). Under atmospheric pressure, decomposition commences at temperatures below 500°, its extent increasing rapidly with the temperature, but the speed with which equilibrium is attained between undecomposed ammonia and nitrogen and hydrogen varies greatly according to the nature of the surfaces with which the gases are in contact. Glass is very inactive, but porcelain and many metals and their oxides have a very strong accelerating effect In presence of the latter decomposition becomes nearly complete at 630° under atmospheric pressure, but the last traces do not disappear even at 1000°. Conversely, in presence of iron as catalyst, Haber and v. Oordt find that at 1000° traces of ammonia are formed from nitrogen and hydrogen at atmospheric pressure, and Nernst and Jost have found that small quantities are formed at the same temperature under the greater pressure at 50–70 atm. At temperatures of 500°-550° under 200 atm. pressure, in presence of metallic osmium or uranium, nitrogen and hydrogen combine to a considerable extent (*see* below).

It has been shown by Regener (Sitzungsber, K. Akad. Wiss. Berlin, 1904, 1228), and by D. Berthelot and Gaudechon (Compt. rend. 1913, 156, 1243), Coehn and Pringent (Zeitsch. Elektrochem. 1914, 20, 275) that ammonia is completely decomposed by ultra-violet light.

Under certain conditions a mixture of air and ammonia gas may be exploded by an electric spark (Schlumberger and Piotrowski, J. Gasbel. 1914, 57, 941). Fires which have occurred in the neighbourhood of refrigerating machines have been attributed to ignition of mixtures of air with ammonia, or, according to Behr, to the ignition of hydrogen formed in the machine by decomposition of ammonia at the high temperature and pressures produced by starting with a closed discharge stop-valve (Cattaneo, Zeitsch. ges. Kalte-Industrie).

Ammonia gas is very soluble in water, alcohol, ether, and many saline solutions, the aqueous solution (caustic ammonia or *liquor ammoniæ*) being of great commercial importance. One gram of water at 0° and 760 mm. absorbs 1148 c.c. or 0·875 gram of ammonia, at 10° 0·679 gram, at 20° 0·526 gram, at 30° 0·403 gram, and at 100° 0·074 gram (Roscoe and Dittmar, Chem. Soc. Trans. 12, 128; Sims, Chem. Soc. Trans. 14, 1; *see* also Perman, Chem. Soc. Trans. 79. 718; 83, 1168). In the act of solution much heat is evolved, and according to Thomsen, $NH_3+aq. = 8430$ cals.

The density of aqueous solutions of ammonia of varying strength is shown in the accompanying table, according to the determinations of Lunge and Wiernik.

DENSITY OF AQUEOUS SOLUTIONS OF AMMONIA AT 15° (LUNGE AND WIERNIK).

Sp.gr.	NH_3 p.c.	1 litre contains NH_3 g.	Correction of sp.gr. for ± 1°	Sp.gr.	NH_3 p.c.	1 litre contains NH_3 g.	Correction of sp.gr. for ± 1°
1·000	0·00	0·0	0·00018	0·940	15·63	146·9	0·00039
0·998	0·45	4·5	0·00018	0·938	16·22	152·1	0·00040
0·996	0·91	9·1	0·00019	0·936	16·82	157·4	0·00041
0·994	1·37	13·6	0·00019	0·934	17·42	162·7	0·00041
0·992	1·84	18·2	0·00020	0·932	18·03	168·1	0·00042
0·990	2·31	22·9	0·00020	0·930	18·64	173·4	0·00042
0·988	2·80	27·7	0·00021	0·928	19·25	178·6	0·00043
0·986	3·30	32·5	0·00021	0·926	19·87	184·2	0·00044
0·984	3·80	37·4	0·00022	0·924	20·49	189·3	0·00045
0·982	4·30	42·2	0·00022	0·922	21·12	194·7	0·00046
0·980	4·80	47·0	0·00023	0·920	21·75	200·1	0·00047
0·978	5·30	51·8	0·00023	0·918	22·39	205·6	0·00048
0·976	5·80	56·6	0·00024	0·916	23·03	210·9	0·00049
0·974	6·30	61·4	0·00024	0·914	23·68	216·3	0·00050
0·972	6·80	66·1	0·00025	0·912	24·33	221·9	0·00051
0·970	7·31	70·9	0·00025	0·910	24·99	227·4	0·00052
0·968	7·82	75·7	0·00026	0·908	25·65	232·9	0·00053
0·966	8·33	80·5	0·00026	0·906	26·31	238·3	0·00054
0·964	8·84	85·2	0·00027	0·904	26·98	243·9	0·00055
0·962	9·35	89·9	0·00028	0·902	27·65	249·4	0·00056
0·960	9·91	95·1	0·00029	0·900	28·33	255·0	0·00057
0·958	10·47	100·3	0·00030	0·898	29·01	260·5	0·00058
0·956	11·03	105·4	0·00031	0·896	29·69	266·0	0·00059
0·954	11·60	110·7	0·00032	0·894	30·37	271·5	0·00060
0·952	12·17	115·9	0·00033	0·892	31·05	277·0	0·00060
0·950	12·74	121·0	0·00034	0·890	31·75	282·6	0·00061
0·948	13·31	126·2	0·00035	0·888	32·50	288·6	0·00062
0·946	13·88	131·3	0·00036	0·886	33·25	294·6	0·00063
0·944	14·46	136·5	0·00037	0·884	34·10	301·4	0·00064
0·942	15·04	141·7	0·00038	0·882	34·95	308·3	0·00065

The solution is very strongly alkaline, and unites with acids to form the ammonium salts, and it is frequently supposed that the solution contains ammonium hydroxide $NH_4·OH$, corresponding to NaOH and KOH. The evidence for this view is not altogether conclusive, and the physical properties of the solution at the ordinary temperature are in some respects opposed to the presence of the compound NH_4OH, and in favour of the supposition that the ammonia is dissolved as such. At very low temperatures, however, Rupert (J. Amer. Chem. Soc. 31, 866; 32, 748) has shown that two definite hydrates exist, the freezing-point curve of mixtures of ammonia and water in varying proportions showing two well-defined minima at −87° and −94° respectively, the composition at these two points corresponding to the formulæ NH_3,H_2O and $2NH_3,H_2O$. The first-named forms small colourless crystals resembling those of sodium and potassium hydroxide; and the latter, larger needle-shaped crystals. Whether these are true hydrates or are to be regarded as ammonium hydroxide NH_3OH and ammonium oxide $(NH_4)_2O$, is at present uncertain.

The aqueous solution of ammonia also dissolves many metallic oxides and hydroxides, such as Ag_2O,$Cu(OH)_2$, as well as many salts which are insoluble in water, such as silver chloride and phosphate, and cuprous chloride, and also acts as a solvent for many fats and resins. The solution of cupric hydroxide in ammonia is of considerable commercial importance, as it is a solvent for cellulose, and is used in large quantities in the manufacture of artificial silk.

I. Technical sources of ammonia.[1] Ammonia is formed in nature chiefly during the decay of nitrogenous organic substances, and consequently exists in considerable quantity both in the soil and the atmosphere. Whilst this is of the greatest importance for agriculture, it is only possible in very exceptional cases to utilise this source for the manufacture of ammonium salts, the greater proportion of the world's production being obtained by the destructive distillation of nitrogenous organic matter, chiefly coal.

A. *Natural occurrence of ammoniacal compounds in quantity of commercial importance.*—Ammonium carbonate has been found in guano deposits on the West Coast of South America, and has been imported into Europe, a sample imported into Germany in 1848 consisting essentially of ammonium bicarbonate mixed with some insoluble matter. Ammonium sulphate is contained in the Tuscan 'soffioni,' and is there obtained in considerable quantity as a by-product in the manufacture of boric acid. Ammonium chloride, together with sulphate, is sometimes found in the neighbourhood of volcanoes.

B. *Synthetic processes for production of ammonia.*—Very many attempts have been made to effect the manufacture of ammonia from atmospheric nitrogen and hydrogen, and a large number of processes with this object have been patented, but until recently, no method which has been proposed has proved successful on a commercial scale, for although, as stated above, nitrogen and hydrogen combine together to a slight extent to form ammonia, when heated together under suitable conditions, the yield at high temperatures was so small that the cost of production would be prohibitive. With many of the methods proposed—such as those of Swindells (Eng. Pat. June 21, 1876), Rickman (Eng. Pat. 3341, 1878), Glover (Eng. Pat. 1890, 1880), Solvay (Bull. Soc. chim. 25, 527), Wagner (Jahresbericht. 1876, 444), Bassett (Eng. Pat. 4338, 1879)—it is very doubtful whether, in fact, any ammonia is produced synthetically, the ammonia obtained being more probably all derived from the nitrogen present in the coal or coke employed in each of these processes. The processes of Johnson (Chem. News, 43, pp. 42, 288), Woltereck (J. Soc. Chem. Ind. 1908, 158, 978; Eng. Pat. 2461, 1902; 16504, 1904; 8358, 1905), Mond (J. Soc. Chem. Ind. 1889, 505), and Roth (D. R. P. 191914), in which a mixture of nitrogen and hydrogen is passed over various heated catalytic agents, do not appear to have resulted in any commercial yield of ammonia. Haber (Zeitsch. Elek. Chem. 16, 244) has found that when a mixture of 1 vol. of nitrogen and 3 vols. of hydrogen is heated with metallic osmium to 550° under a pressure of 200 atm., a very considerable production of ammonia takes place amounting to 8 p.c. of the mixed gas, and although osmium is too scarce and expensive for technical use, it may be replaced by metallic uranium with good results. With a small apparatus constructed to allow of the circulation of the mixed gas under this pressure over uranium heated to about 500°, and cooling between each passage of the gas over the metal, Haber has synthesised ammonia at the rate of about 90 grams per hour, the ammonia separating out on cooling under these conditions as a liquid.

The Haber process has now been developed on a very large scale by the Badische Anilin und Soda Fabrik, and it is stated that in 1918 a quantity of ammonia equivalent to 400,000 tons of ammonium sulphate was manufactured by this method (Eng. Pats. 17642, 17951, 1909; 10441, 13097, 15975, 19249, 19778, 20127, 1910; 61, 5833-6, 21151, 24657, 25252, 28167, 1911; 1161, 3345, 9841, 22352, 25259, 1912; 24823, 1913; 8763, 1915). The work done by them has especially consisted in the design and construction of suitable plant to withstand the combined high temperatures and high pressures necessary for successful working, and the selection of suitable catalysts of less expensive character than the osmium and uranium employed in the small scale experiments. No details of the exact construction of plant or of the actual catalyst now employed have been published, but Benthsen (Zeitsch. angew. Chem. 1913, 10) states that the more expensive forms of the latter first used can be replaced by cheaper metals such as iron, manganese, and molybdenum, which are 'activated' by the addition of other substances. Contact 'poisons' both in the catalyst itself and in the mixture of nitrogen and hydrogen used must be very completely excluded; the following substances especially having proved very deleterious: sulphur, selenium, tellurium, phosphorus, arsenic, boron, some hydrocarbons, and the readily fusible metals or their oxides, such as lead, bismuth, and tin. Much experimental work on the direct synthesis of ammonia from nitrogen and hydrogen has been carried out in Great Britain during the last few years, both on the laboratory and on a semi-industrial scale, the results of which have only been partially published (*see* Maxted, Chemical Age, 1919, 1, 514, 540, 590). Up to the present (1919) no plant has been erected for the production of ammonia by this method in this country.

Attempts to effect the synthesis of ammonia from a mixture of nitrogen and hydrogen by the passage of the silent discharge or sparks have failed to give a sufficient yield for commercial success, and a similar lack of success long attended the efforts to produce ammonia by combining atmospheric nitrogen with elements which readily form nitrides, such as boron, titanium, magnesium, and subsequent conversion of the nitride into ammonia by the action of steam. Recently, however, Serpek and the Soc. Gen. des Nitrures (Eng. Pats. 13579, 1906; 7507, 15995-7, 1909; 13086, 1910; 23544, 25141, 1911; 8347-9, 10036, 22435, 25630, 1912; 10975, 11091, 21366, 23740, 24731, 27030, 27971, 1913; 4287, 22586, 24533, 1914) have developed a process dependent on the formation of aluminium nitride by the action of carbon and nitrogen on alumina at high temperatures, and subsequent conversion of the nitride into ammonia, with recovery of the alumina, by heating with water under pressure. To carry out the process, bauxite, which reacts more readily than pure alumina, is preheated to a temperature of about 1600° and passing through a revolving electric carbon-resisting furnace, the nitrogen being supplied from a current of producer-gas passing through the furnace in the opposite direction to the flow of bauxite. The crude nitride is then heated under pressure with dilute alkali, which effects the conversion into ammonia much more readily than water. A number of plants working this process are being erected in France by the Soc. Gen. des Nitrures.

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[1] For more complete details, *see* Lunge's Coal-Tar and Ammonia (Gurney and Jackson, 1916).

C. *Production from cyanides.*—It has long been known that nitrogen combines at high temperatures with carbon and alkalis with production of cyanides, and many attempts have been made during the last fifty years to manufacture cyanides in this manner and to convert these subsequently into ammonia by the action of superheated steam. The large demand for cyanides themselves, resulting from their employment in the extractions of gold from the mine tailings, and the fact that at present nitrogen, in the form of cyanide, commands a higher price than in the form of ammonia, has made such processes of no value for ammonia production under existing conditions, and in fact, at the present time, the opposite process of converting ammonia into cyanides is carried on to a large extent. The methods proposed, so far as they relate to cyanide production, will be discussed under that heading, but one method may be here mentioned, namely, the manufacture of calcium cyanamide, $Ca:N{\cdot}C\vdots N$, according to Frank and Caro's process (J. Soc. Chem. Ind. 1908, 1093), by the action of nitrogen on heated calcium carbide, this being simultaneously a cyanogen and an ammonia derivative (*v. Cyanamide*, art. NITROGEN, ATMOSPHERIC, UTILISATION OF). This substance may readily be converted into ammonia by the action of superheated steam, but it is for the most part directly employed on the land as a nitrogenous manure.

D. *Ammonia from urine, sewage, and animal excreta.*—Urine is not merely the oldest, but for centuries was the only source of obtaining ammonia compounds on a commercial scale. It is stated that sal-ammoniac made from it was an article of commerce as early as 1410, and that the Jesuit Sicard in 1720 saw the manufacture of it in the Delta of the Nile. In Egypt sal-ammoniac was made by burning camels' dung and collecting the sublimate. Putrefied urine (in which the urea has passed into ammonium carbonate) has been used for centuries, and to a certain extent is still used by dyers as a source of ammonia for scouring wool and other purposes.

Normal urine contains per litre from 20 to 35 grams urea (carbamide), which after a short time is changed into ammonium carbonate under the influence of a micro-organism. An adult man produces from 22 to 37 grams urea per 24 hours, together with a little uric acid, corresponding to 12·5–21 grams NH_3 per day, or between 9 and 17 lbs. per annum. If all the ammonia obtainable from London urine were recovered this would amount to 100,000 tons of ammonium sulphate per annum.

Owing to the now almost universal adoption of the removal of sewage by means of water, the dilution of the ammonia in the combined sewage is so great that its recovery is hardly practicable, but with concentrated pan sewage, recovery of ammonia is carried on in a few places, especially in Paris. A large number of patents have been taken out for the recovery of ammonia both from sewage and also from the more concentrated sludge deposited in the collecting tanks at the sewage works, among which may be mentioned Duncan (D. R. PP. 27148, 28436), Young (Eng. Pat. 3652, 1882), Bolton and Wanklyn (Eng. Pat. 5173, 1880), Gesellschaft für Wasserabklärung, Berlin (D. R. P. 161166), Butterfield and Watson (Eng. Pat. 19502, 1905), Taylor and Walker (U.S. Pat. 603668).

Ketjen (Zeitsch. angew. Chem. 1891, 294) also reports a successful recovery of ammonia from concentrated sewage by distillation with lime at Amsterdam.

E. *Ammonia from guano, &c.*—Whilst the ammonia obtainable from excreta is mostly lost for immediate recovery, as it quickly passes away into the water, the soil, or the air, there are a few exceptions to this rule presented by the deposits of birds' excrements on some desert islands, and a few similar cases. In this 'guano,' ammonia salts exist already preformed, and ammonia can be formed from other nitrogenous substances contained therein by heating guano with lime (as patented by Young in 1841), but this process is not remunerative, since the direct manurial value of guano is much superior to that of the ammonia salts obtainable therefrom.

F. *Manufacture of ammonia by the destructive distillation of nitrogenous organic matter.*—The total quantity of ammonia commercially produced by more of the methods described above is at present almost negligible, nearly the whole of the world's supply of ammonia and its salts being obtained either as a by-product in the course of other manufactures in which nitrogenous organic matter is subjected to the process of destructive distillation, or manufactured synthetically from nitrogen and hydrogen. Much the greatest proportion is obtained in the manufacture of illuminating gas, power gas, or coke from coal, and in the distillation of shale for the production of shale oil. A considerable amount is also recovered from the gases evolved from blast-furnaces where coal is used as fuel, and smaller quantities from the distillations of bones, horn, and other animal refuse, and also from the residue obtained from beet-root molasses.

The total production of ammonia in the United Kingdom, calculated as sulphate, for the year 1913, previous to the outbreak of war, and for 1917 and 1918, is shown in the following table, the figures for 1889 being also given to indicate the increase in production during the past 30 years. The statistics are taken from the Annual Reports of the Chief Alkali Inspector:—

	1889	1913	1917	1918
Gas works	87,000	182,180	188,478	173,541
Iron works	5,500	19,956	13,621	12,717
Shale works	22,000	63,061	60,560	58,311
Coke ovens	—	133,816	166,354	164.448
Producer gas and other carbonising works	3,000	33,605	29,604	23,534
	117,500	432,618	458,617	432,551

The world's production for 1907, 1910, and 1913 (in metric tons of 2204 lbs.) is estimated as follows:—

	1907	1910	1913
Great Britain .	331,220	369,000	438,932
Germany . .	287,000	383,000	549,000
United States .	81,400	116,000	176,900
France . .	52,700	57,000	75,400
Belgium and Holland . .	55,000	41,000	48,600
Other countries .	88,000	145,800	123,200
	895,320	1,111,800	1,412,032

Coal always contains nitrogen in greater proportion than is present in fresh vegetable matter, this being probably due to the remains of animals inhabiting the coal-forming forests and swamps. The total percentage of nitrogen found in the coal usually varies between the limits of 0·9 and 2·0 p.c.; thus Tidy (Lunge's Coal Tar and Ammonia) found in Welsh coal 0·91 p.c., in Lancashire coal 1·25 p.c., and in Newcastle coal 1·32 p.c., whilst Foster (Inst. Civ. Eng. 77, iii. 23) found in Welsh anthracite 0·91 p.c., in English coals 1·66–1·75 p.c., and in Scotch cannel 1·28 p.c. Schilling (J. Gasbel, 1887, 661), using the Kjeldahl method of estimation, obtained from Westphalian coal 1·50 p.c., from Saar coal 1·06 p.c., from Silesian coal 1·35 p.c., from Bohemian coal 1·36 p.c., from Saxon coal 1·20 p.c., from Boldon (Durham) coal 1·45 p.c., from Pilsener cannel 1·49 p.c., and from Bohemian lignite 0·52 p.c. McLeod (J. Soc. Chem. Ind. 1907, 137) analysed 80 samples of Scotch coals and cannels, and found percentages of nitrogen varying from 0·91 to 1·87, and averaging 1·43.

The world's production of coal in 1909 amounted to about 950,000,000 tons, containing on the average probably some 1·3 p.c. of nitrogen, which, if the whole were recovered as ammonia, would represent an output of about 48,000,000 tons of ammonium sulphate per annum. In fact, however, the production, as shown by the above figures, only amounts to about $\frac{1}{50}$ of this quantity. Fully 90 p.c. of the coal is consumed in such a manner that the recovery of the nitrogen is impracticable, and where the processes in use are mostly such that ammonia is recovered, only a relatively small proportion of the nitrogen is actually obtained in the form of ammonia, for reasons discussed later in considering the different manufactures in which it is produced.

(*a*) *Production o ammonia in the manufacture of coal gas, and of coke in by-product coke ovens.*—In this country the carbonisation of coal in retorts for the manufacture of illuminating gas for general distribution at present yields the largest contribution of ammonia, but the output from this source is being rapidly approached by that obtained in the analogous process of carbonising the coal in ovens for the manufacture of hard metallurgical coke. Formerly the great bulk of such coke was manufactured in beehive ovens, in which case no by-products were recovered, but these are now being rapidly replaced by by-product recovery ovens. In Germany and in the United States by far the largest proportion is obtained from coke ovens.

In both industries, however, only a portion of the nitrogen of the coal is recovered in the form of ammonia, the remainder being distributed in the coke, as nitrogenous compounds in the tar, as cyanide in the gas and ammoniacal liquor, and as free nitrogen in the gas. The relative proportion of the nitrogen obtained in the different forms varies considerably, being dependent both on the nature of the coal and on the conditions of carbonisation; the rate at which the latter proceeds, and especially the temperature employed have a marked influence. At low temperatures, such, for example, as are employed in the manufacture of 'coalite' (about 450°), a very large proportion of the nitrogen remains in the coke, but with higher temperatures, although more nitrogen is given off from the coke primarily in the form of ammonia, this is partly converted into hydrocyanic acid by the action of incandescent carbon and partly dissociated into its elements, the latter being especially the case when the volatile products as well as the residual coke are strongly heated.

The maximum yield of ammonia, when coal is carbonised in horizontal retorts or in ovens, appears to be obtained with a carbonising temperature of 900°–950°, and the normal production calculated as sulphate is usually from 20–25 lbs. per ton of coal carbonised in such plant. With vertical retorts, with even higher carbonising temperatures, a higher yield is obtained, as in spite of such higher temperatures, the volatile products can escape from the action of heat without being raised to so high a temperature as is the case in horizontal retorts or ovens. Where the charge in the vertical retorts is steamed during carbonisation to increase the water-gas production in the retort, still higher production of ammonia is obtained, and the yield may then amount to 40–50 lbs. of sulphate per ton of coal.

Many attempts have been made to increase the proportion of nitrogen converted into ammonia, but none applicable to these two industries has had any success. Cooper's lime process (Eng. Pat. 5713, 1882), in which lime is added to the coal before carbonisation, was tried in many works, and abandoned, as, although a greater yield of ammonia was obtained, the gain in this respect was more than counterbalanced by the loss due to depreciation in the quality of the resulting coke.

The following tables, which give figures obtained over a long period of working in gas-works and coke ovens respectively, probably represent a fair average of the distribution of the nitrogen in the two industries under modern conditions, although doubtless in different works considerable variations from these figures occur. The gas-works figures are given by McLeod (J. Soc. Chem. Ind. 1907, 137) as the result of working at the Provan Gas Works, Glasgow, and the coke-oven figures by Short (J. Soc. Chem. Ind. 1907, 581) for the working of Otto-Hilgenstock Coke Ovens, using Newcastle coal.

	Gas works	Coke ovens	
Nitrogen in coke .	58·3 .	43·31	p.c. of total
„ in tar .	3·9 .	2·98	„
„ as ammonia	17·1 .	15·16	„
„ as cyanide .	1·2 .	1·43	„
„ as free nitrogen in the gas	19·5 .	37·12	„

McLeod does not appear, however, to include in his cyanide figures the hydrocyanic acid removed from the gas during condensation, allowance for which would probably raise the cyanide figure to about 1·5 p.c.

In both gas and coke-oven works the ammonia is recovered by cooling the gas, when tar and aqueous vapour condense, the condensed water removing a large portion of the ammonia and other gaseous impurities from the gas, and the remainder being recovered by washing the cooled gas with water. Recently, also, especially in coke-oven works, processes have been adopted in which the ammonia is directly recovered from the hot gas by washing with sulphuric acid after removal of the tar. Methods for manufacturing ammonium sulphate direct from the crude gas, in which the sulphuretted hydrogen present is simultaneously oxidised to form the necessary sulphuric acid, have been described by Feld (Eng. Pat. 3061, 1909) and Burkheiser (Eng. Pat. 20920, 1908; 21763, 1908; 17359, 1910), but the processes are still (1910) in the experimental stage.

The various apparatus employed and methods of working are described in the articles on Gas (Coal) and Coke.

(*b*) *Production of ammonia in the manufacture of producer gas from coal.*—In the manufacture of producer gas from carbonaceous fuel (*see* Gas, Producer) by the introduction of limited amounts of air and steam into the incandescent fuel, the whole of the carbon of the latter is gasified together with the nitrogen it contains. Where the quantity of steam added is limited, so as to ensure that the gas produced shall only contain small percentages of carbon dioxide, the temperature of the producer is such that almost the whole of the ammonia formed from the nitrogen is dissociated into its elements as fast as it is produced. If, on the other hand, a large excess of steam is employed, the temperature of the producer is so much lowered that the greater part of the ammonia escapes decomposition, and may then be recovered from the gas evolved. The latter contains much larger percentages of hydrogen and carbon dioxide than that obtained by the use of smaller quantities of steam, but is still capable of economic employment, especially in gas engines. The process is therefore now largely adopted for producers using bituminous fuel, especially in the Mond Gas plant, in which up to about 75 p.c. of the nitrogen in the coal is recovered as ammonia. This is usually obtained direct as sulphate by washing the crude gas with dilute sulphuric acid, and subsequent evaporation and crystallisation of the solution obtained; the sulphate thus produced has, however, generally a yellow or brownish colour, due to the presence of small amounts of tarry matter.

The use of such large proportions of steam is impracticable in gas works or coke ovens where gas of high calorific power or coke of good quality or both is required, but with the lower grade of calorific power now manufactured, a moderate proportion of steam may be admitted without undue reduction of the calorific power, and results, as mentioned above, especially with vertical retorts, in the production of greater yields of ammonia.

(*c*) *Production of ammonia from shale.*—In the distillation of Scotch bituminous shales for the production of shale oil (*see* Paraffin), ammonia is also evolved, and is recovered in a similar manner to that employed in gas works. In this case also the introduction of steam (and also of limited quantities of air) during the distillation has the effect of largely increasing the percentage of nitrogen recovered as ammonia. The objections to the method which hold in the case of the gas industry do not apply in the shale-oil manufacture, as the chief product, the shale oil, is not materially affected by the use of steam, and the coke formed is in any case of little value. The gas produced, even when steam is used, is sufficiently good for the purpose for which it is used, namely, for heating the retorts. The addition of steam for increasing the yield of ammonia was, in fact, first worked out to practical success in this industry, chiefly by Young and Beilby (Eng. Pat. 1587, 1881; 2164, 1881; 4284, 1881; 1377, 1882; 5084, 1882; see also Beilby, J. Soc. Chem. Ind. 1884, 216), its application in the case of carbonisation of coal in producers for the same purpose being of rather later date.

(*d*) *Ammonia from blast furnaces.*—Where coal is used as fuel in blast furnaces for cast-iron production, the waste gases contain considerable quantities of ammonia and tarry matters, which are now largely recovered from the gas, the latter, after purification, being employed in gas engines. In most English districts, the coal available is not sufficiently hard for use in the furnaces, and hard coke is used, the employment of coal being confined chiefly to the West of Scotland and to North Staffordshire, where coal of sufficient hardness can be obtained. The recovery of the tar and ammonia is effected by cooling and washing in a similar manner to that employed in gas works, the apparatus being suitably modified to allow for the fact that the tar and ammonia are much more diluted with other gases, and that large quantities of dust are mechanically carried along with the gas from the blast furnace. Processes for the washing of the gas with dilute sulphuric acid do not appear so far to have been permanently successful, and the same is true of the process of Addie (Eng. Pat. 4758, 1882; 3246, 1883), in which the gas was mixed with sulphur dioxide and passed through a scrubber fed with water, the resulting solution of ammonium sulphite being oxidised to sulphate by injection of air.

The yield of ammonium sulphate obtained from blast furnaces is very similar to that obtained in gas works and from coke ovens, namely from 20 to 25 lbs. per ton of coal.

(*e*) *Ammonia from peat.*—Vast deposits of peat exist in many places, especially in Ireland and Prussia, and as this contains a good deal of nitrogen, amounting in some cases to 4 p.c. of the dry peat, many attempts have been made to recover this nitrogen as ammonia. The great difficulty in the way has been the very large quantity of water contained in the peat, which is costly to remove, and hitherto very little ammonia has been put on to the market from this source. Of the earlier attempts that of Grouven (D. R. PP. 2709, 13718, 18051) is of interest, inasmuch as this represents one of the first attempts to increase the yield of ammonia by injection of steam during distillation, but although prolonged experiments were made with the process, it was ultimately abandoned. Lencauchez suggested the use of peat in gas producers with subsequent ammonia recovery, and patents relating to the matter were taken out by Ruderer, Loe, and Gumbart (D. R. P. 53844), Kuntze (Eng. Pat. 9052, 1891), and Pieper (Eng. Pat. 28190, 1896); Woltereck (Eng. Pat. 16504, 1904; 28963, 1906; 28964, 1906).

Frank and Caro, in conjunction with the Mond Gas Co. (Zeitsch. angew. Chem. 1906, 1569), find that peat containing 50 p.c. of water may be employed in place of coal in the Mond Gas plants, with production of gas suitable for gas engines, and a yield of about 90 lbs. of ammonium sulphate per ton of dry peat.

(*f*) *Ammonia from bones, horn, leather, hair, skins, and other animal refuse.*—In the distillation of bones for the manufacture of bone charcoal (animal charcoal, or 'char'), used especially in sugar refining, large quantities of ammonia are formed, together with tar rich in pyridines, known as 'Dippel's oil.' The carbonisation is frequently carried out, especially in France and Germany, by heating the bones in open pots placed in a furnace, in which case the tar and ammonia are so largely diluted with hot furnace gases that their recovery is rendered very difficult. In this country generally, and to an increasing extent elsewhere, the carbonisation is effected in closed retorts, and the tar and ammonia recovered in accordance with the usual gas works practice, the yield of ammonia being equivalent to about 50–60 lbs. of sulphate per ton of dry bones.

Other animal refuse, such as wool, hair, skin, waste leather, &c., is sometimes carbonised in a similar way, the residue being employed as manure, and the ammonia recovered from the gases. Sometimes, however, these materials are simply heated in cylinders in a current of steam, which renders them friable and capable of ready disintegration, when they are directly employed as manure. A further proposal is to utilise the nitrogen by heating the dried refuse with concentrated sulphuric acid, whereby the nitrogen is converted quantitatively into ammonium sulphate, as in the well-known Kjeldahl method of estimating nitrogen.

(*g*) *Ammonia as a by-product in the beet-root sugar industry.*—During the evaporation of beet-root juice, small amounts of ammonia are evolved, which Vibrans (D. R. P. 15513) has proposed to collect. Much larger amounts can, however, be obtained by the distillation of the 'vinasse,' *i.e.* the residue left after fermenting the sugar remaining in the molasses, and distilling off the alcohol produced. This contains nitrogenous bases, especially betaïne, and on dry distillation yields ammonia and trimethylamine. Vincent (Chem. News, 39, 107) carried out the distillation with the primary object of obtaining trimethylamine and from the latter methyl chloride, but the ammonia was simultaneously recovered as sulphate. The residue from the distillation is rich in potassium salts, and is employed as a manure or worked up into pure salts. Other patents dealing with the recovery of ammonia by distillation of vinasse are those of Ernst (D. R. P. 13871), Lederer and Gintl (D. R. P. 17874), and Meyer (Eng. Pat. 17347, 1887). Bueb (Eng. Pat. 7175, 1895; 26259, 1898; see also Ost, Zeitsch angew. Chem. 19, 609) utilises the vinasse for the production of both ammonia and cyanides, the latter being the product especially aimed at. In his process the vinasse is carbonised in retorts in the ordinary manner, and the gases, which contain ammonia and trimethylamine, but little hydrocyanic acid, are then passed through a highly heated brickwork chamber, the ammonia being only slightly affected, whilst the trimethylamine is converted chiefly into hydrocyanic acid. The resulting gases, containing about 7 p.c. of ammonia and 7 p.c. of hydrocyanic acid, are passed through sulphuric acid to recover the ammonia as sulphate, and the gas freed from ammonia employed for the manufacture of cyanide.

II. **Properties and Composition of Ammoniacal Liquor.** The ammoniacal liquor obtained by the washing and cooling of the gases produced by destructive distillation, is, after separation from tar by settling, a liquid having a colour from pale yellow to dark brown, and smelling strongly of ammonia, sulphuretted hydrogen, and also of phenols. Its specific gravity usually varies from 1·01 to 1·03. In the coal-gas manufacture, the liquor is usually obtained in three stages, viz. (1) the hydraulic main liquor, formed during the cooling of the gas to temperatures of 50°–60°, which is usually weak (0·5–1·0 p.c. of NH_3), owing to the lessened solubility of ammonia at that temperature; (2) the condenser liquor, produced in the subsequent cooling of the gas to atmospheric temperature, which is more concentrated (2–3·5 p.c. of NH_3); and (3) the scrubber and washer liquor, formed by washing the cooled gas to effect complete removal of the ammonia, the strength of which varies considerably, and depends largely on the construction of the washing plant, and the supervision of the working. The first two products together form the 'virgin liquor,' *i.e.* solution produced from the water formed by the condensation of the steam always present in the crude gas; but the liquor from all sources is usually collected together with the tar in a common storage well or wells. Frequently the weak hydraulic main liquor is used, after cooling, in the preliminary washers or scrubbers, thereby effecting a further partial removal of the ammonia, and becoming simultaneously concentrated, but for the complete removal of the ammonia the gas must be washed with fresh water in the final scrubber. In coke-oven works the conditions prevailing in these respects are very similar generally to those in gas works.

The quantitative composition of the ammoniacal liquor varies considerably, not only in that obtained at different stages of the process, but also in the average liquor obtained, being dependent on the nature of the coals carbonised, the conditions of carbonisation, and the construction and working of the condensing and scrubbing plant. The qualitative composition varies but little; the primary products formed in the liquor are ammonium chloride, sulphides, carbonates, and cyanide, produced by the action of the ammonia solution on the acid constituents of the crude gas, viz. hydrochloric acid, sulphuretted hydrogen, carbon dioxide, and hydrocyanic acid. The strongly acid hydrochloric acid is absorbed in the earlier stages of the cooling, chloride being only present to any extent in the hydraulic main and condenser liquor, but the total quantity of ammonia present is insufficient to remove the whole of the remaining acid gases, which are separated later by special purification processes. Other ammonium salts are, however, produced in the liquor by secondary reactions; thus the sulphide is oxidised by the oxygen always present in the crude gas, and later by the oxygen of the air to which it is exposed during storage, yielding polysulphides, thiosulphate, sulphate, and possibly sulphite. The cyanide reacts with the polysulphide, forming thiocyanate, and possibly also with thiosulphate, forming thiocyanate and sulphite, so that polysulphide is rarely found in the liquor. Small quantities of ferrocyanide are also sometimes formed by the action of ammonium cyanide on the ironwork of the apparatus. In addition, the liquor always contains small quantities of pyridine, and considerable amounts of substances derived from the tar, especially phenols.

From the point of view of the subsequent working up of the ammoniacal liquor, it is important to distinguish between the amount of 'volatile' and 'fixed' ammonia present. The former represents the ammonia present as sulphide, carbonate, and cyanide, and in combination with the phenols, the term being given because the ammonia in this form is completely dissociated and volatilised by simply boiling the solution; whereas that present as chloride, sulphate, thiosulphate, and thiocyanate is not evolved to any material extent under these conditions, and is therefore termed 'fixed' ammonia. For its recovery it is necessary to add to the liquor a sufficient amount of a stronger alkali to combine with the whole of the above-named acids present. The 'fixed' ammonia in the average liquor usually amounts to from 20 to 25 p.c. of the whole, but the proportion is much higher in the hydraulic main and condenser liquor.

COMPOSITION OF AMMONIACAL LIQUOR.

—	Gas works					Coke ovens	Blast furnaces		Shale works	Coalite works	—
	Average of five samples of stored liquor.—English works	Stored well liquor.—German works	Hydraulic main liquor.—English works	Hydraulic main liquor.—German works	Condenser liquor.—English works	Average of nine samples of liquor	Liquor from coolers only	Liquor from washers only	Average liquor from storage well.	Average liquor circulated through washers to get up strength	
Volatile ammonia . .	1·929	1·406	0·721	0·291	8·247	0·841	0·191	0·362	0·873	1·547	grams per 100 c.c.
Fixed " . .	0·618	0·309	0·306	0·288	0·221	0·102	0·008	0·009	0·032	0·170	"
Total " . .	2·542	1·715	1·027	0·579	3·468	0·943	0·199	0·871	0·905	0·717	"
Ammonium sulphide $(NH_4)_2S$	0·862	0·276	0·276	0·073	0·768	0·466	nil	?	0·098	0·230	"
" carbonate $(NH_4)_2CO_3$	5·000	3·526	1·320	0·475	8·810	1·960	1·104	?	2·870	6·360	"
" chloride NH_4Cl	1·120	0·738	0·838	0·722	0·459	0·217	0·006	?	0·015	0·106	"
" sulphate $(NH_4)_2SO_4$	0·202	0·023	?	0·023	?	0·032	0·009	?	0·016	0·054	"
" thiosulphate $(NH_4)_2S_2O_3$	0·173	0·123	?	0·143	?	0·041	0·002	?	0·090	0·407	"
" thiocyanate NH_4CNS	0·528	0·182	0·047	0·100	0·070	0·043	0·003	0·003	nil	0·335	"
" cyanide NH_4CN	0·036	0·003	0·034	0·003	0·070	0·070	nil	0·003	nil	nil	"
" ferrocyanide $(NH_4)_4Fe(CN)_6$	0·038	0·088	0·019	0·019	0·030	nil	nil	nil	nil	nil	"
Authority . . .	Linder	Mayer and Hempel	Linder	Mayer and Hempel	Linder	Linder	Linder	Linder	Linder	Linder	

The quantity of phenols present in gas-works liquor usually varies from 0·1 to 0·35 gram per 100 c.c. (Skirrow, J. Soc. Chem. Ind. 1908, 58).

The above table gives the results of a number of analyses of ammoniacal liquor from gas-works, coke-ovens, shale-works, and iron-works, made by Linder, on behalf of the Chief Alkali Inspector, and published in the annual reports of the latter. In addition an analysis is also given of the liquor obtained in low-temperature carbonisation as practised in the coalite manufacture, and two analyses of German gas-works liquor, by Mayer and Hempel (J. Gasbel, 1908, 428). (For methods of analysis, *see* Linder (Alkali Inspector's Report, 1909, 15), and Mayer and Hempel (*l.c.*).) In these analyses the whole of the carbon dioxide and sulphuretted hydrogen present is calculated as the normal carbonate and sulphide respectively, and in Linder's analyses the difference between the total sulphur and that present as sulphide, sulphate, and thiocyanate is calculated as ammonium thiosulphate.

The existence of free ammonia (or its

hydroxide) is a point on which considerable difference of opinion exists. The above analytical results appear to show that in the case of average stored liquor, the quantity of acids present, including phenol, is usually sufficient to combine with the whole of the ammonia but at the same time it is very probable that some of the salts, especially the sulphides and carbonates, undergo hydrolytic dissociation into acid and free ammonia or its hydroxide in the solution. With the hydraulic main liquor, formed at temperatures mostly above 60°, the acids found are insufficient to combine with the whole of the ammonia, some of which must therefore be present in the free state. The existence of free ammonium cyanide in the liquor has also frequently been denied, but more perfect methods of analysis have shown that this is undoubtedly often present in small quantity even in stored gas-works liquor, and that in coke-oven liquor, which is usually only stored for a short time before working up, the amount may be considerable. The presence of cyanide is objectionable, as it increases the amount of hydrocyanic acid in the waste gases from the manufacture of ammonium sulphate (*see* below).

III. Valuation of Ammoniacal Liquor. In this country, for technical purposes, the strength of the ammoniacal liquor is mostly expressed in terms of 'ounce-strength,' this figure representing the number of ounces avoirdupois of pure sulphuric acid required to neutralise the ammonia contained in 1 gallon of the liquor, and for statistical purposes or sale, the volumes of liquor are usually converted into the equivalent volume of liquor of 10-oz. strength. In order to convert these figures into the more generally familiar ones of grams per 100 c.c., the 'oz.-strength' figures must be multiplied by 0·217, and conversely, to convert figures representing grams per 100 c.c. into oz.-strength, the former must be multiplied by 4·61.

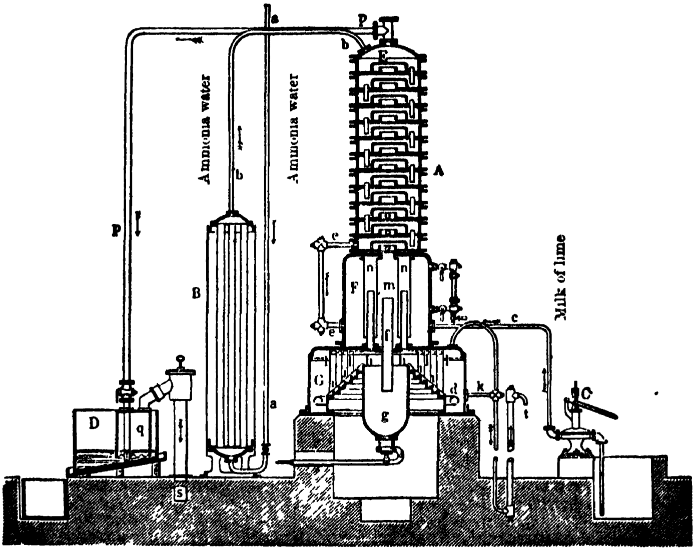


Fig. 1.

For approximate purposes the ammonia content of the liquor is frequently estimated from the density, it being found that each 1° Twaddell corresponds roughly to 2-oz. strength. This approximation is sufficient for such purposes as the control of the daily working of the washers and scrubbers on the works, but quite unsuitable for purposes where fair accuracy is desired, as a liquor showing 5°Tw., for example, may vary in actual content from 8- to 12-oz. strength, as against the supposed 10-oz. For any but the roughest purposes, ammonia is estimated by the usual method of distilling a known volume, after addition of alkali to decompose the fixed salts, collecting the distillate in excess of standard acid, and titrating the unused acid with standard alkali. The liquid must not be distilled to dryness, as otherwise the thiocyanates may be decomposed with formation of ammonia, giving too high results.

IV. Working up of Ammoniacal Liquor. In the earlier days of the utilisation of gas liquor, this was simply neutralised with sulphuric or hydrochloric acid, and the resulting solution evaporated, but the products obtained were very impure, containing tarry matter and thiocyanate, and the escaping gases, especially the sulphuretted hydrogen, created great nuisance. At present the ammonia is almost invariably recovered from the liquor in the first instance by distillation. Formerly, also, in many cases, only the volatile ammonia was recovered, as this could be obtained without addition of alkali, the fixed ammonia being run off with the waste liquor; but this procedure is now becoming exceptional, the fixed ammonia, except in the case of some small plants, being also mostly recovered by addition of the necessary alkali. On account of its cheapness, lime is almost always employed for this purpose, but in some small plants, caustic soda is used, for although the cost of the latter is much greater, this is held by some makers to be compensated for in such plants by the fact that the stills run much longer without cleaning.

The plant employed in the distillation has been of various types; at first an intermittent process of distilling the liquor in externally fired boilers was adopted, the distillation being continued until the whole of the volatile ammonia was expelled with the steam. Addition of lime to drive off the fixed ammonia was rarely practised with such plants, owing to the formation of thick deposits of lime salts on the heated boiler plates. These plants have now been almost entirely superseded by continuous column stills, constructed on the general principle of the Coffey still, the intermittent system being now employed only in very small works or in special cases, such as the distillation of liquors containing very large quantities of fixed ammonia, in which case the addition of the necessary amount of lime renders the liquid so thick that these must be stirred by mechanical agitators to effect complete recovery of the ammonia. The annual report of the Chief Alkali Inspector for 1909 shows that in the various districts into which the United Kingdom is divided for administration purposes under the Alkali Act, the proportion of liquor distilled by intermittent stills varies from about 7 p.c. to *nil*, and probably averages over the whole country from 1 to 2 p.c.

For the purpose of heating the stills, three methods have been employed: (1) external firing; (2) by means of internal coils through which steam is passed; and (3) by blowing live steam through the stills. The first plan gives a high fuel consumption, as well as trouble from lime deposits on the heated portions of the still; and of the other two methods the use of live steam is the most economical in fuel consumption, and is therefore now almost invariably adopted.

The ammonia evolved on distillation is converted at once either into ammonium sulphate, concentrated gas liquor, pure aqueous ammonia, or liquefied ammonia. The remaining salts of commercial importance, namely, ammonium chloride, carbonate, and nitrate, are now rarely manufactured directly from the ammonia as evolved from the stills, but are obtained either from ammonium sulphate or aqueous ammonia previously prepared from the gas liquor. Much the largest proportion of the liquor is converted into sulphate, the demand for this salt being greatest, owing to its employment as a nitrogenous manure. The method of manufacture of this salt will therefore be described first, followed by that of the other commercially important ammonia derivatives.

Ammonium sulphate.—A description of the different forms of intermittent still formerly adopted for obtaining the ammonia in the liquor, but now seldom used, may be found in Lunge's Coal Tar and Ammonia 4th ed. Of the continuous stills, those of Grüneberg and Blum (D. R. P. 33320) and of Feldmann (Eng. Pat. 3643, 1882) will be described, more recent forms differing from these only in detail and not in general principles. In the manufacture of sulphate, the volatile ammonia is first driven off, lime being then added to the liquor to liberate the fixed ammonia, the combined gases evolved being passed through sulphuric acid.

The apparatus of Grüneberg and Blum is shown in Fig. 1, as arranged for the manufacture of sulphate. A is the still, B the gas-liquor heater or economiser, C the lime pump, and D the saturator charged with acid for absorption of the ammonia. The gas liquor enters the economiser B by means of pipe *a*, and is heated by the hot waste gases from the saturator, and passes thence by the pipe *b* to the top of the column E of the still. This column is divided into a number of compartments by horizontal division plates, the liquor flowing downwards from compartment to compartment by the overflow pipes, the admitted steam travelling upwards in the reverse direction through the central pipes *o*, covered by hoods having serrated edges, which compel the steam to bubble through the liquor in each compartment, thus driving off the 'volatile' ammonia and also the volatile acids present, viz. carbon dioxide, sulphuretted hydrogen, and hydrocyanic acid.

The lime vessel F, into which milk of lime is pumped by means of pump C and pipe *c*, serves to expel the fixed ammonia, and the boiler G, with its stepped cone, serves to boil the liquor in thin sheets, by means of the steam coil *d*, and thus to set free the last portions of ammonia. In B the first heating of the liquor takes place by means of the hot vapours from the saturator D, which ascend through the bell *q*, the pipe *s*, and the inner pipes of B, while the liquor, arriving at *a*, rises up in B. It then enters through *b* into the dephlegmating column E, and finds its way downward from chamber to chamber, till it gets into the lime vessel F. From here it overflows by pipe *f* into the sludge-catcher *g*, overflows here again all round at *hh*, and runs over the cone *i* downwards from step to step; from the pipe *k* it is discharged continuously and quite spent to the overflow *l*. The steam travels in the opposite way—namely, along the steps of cone *i*, upwards in pipe *m*, and through *n* into the lime vessel F. From here the mixed steam and ammonia vapours ascend into the column E, and traverse this from chamber to chamber, and ultimately leave it by the pipe *p*. This pipe enters the saturator D, charged with sulphuric acid. The sulphuretted hydrogen, carbon dioxide, &c., collecting in the bell *q*, are led through the flue *s* into the economiser B, where they give up their heat to the gas liquor, and lose their steam in the shape of condensed water. Ultimately they are conveyed away by a pipe not shown in the diagram for treatment to prevent nuisance, the methods adopted for the purpose being described below.

In the apparatus of Feldmann (D. R. P. 21708), Fig. 2, the gas liquor, after having passed through the ordinary rectifying column A, flows into a vessel B, into which milk of lime is pumped by G in regular intervals, whilst the whole is kept agitated by steam injected into the mixture. The liquor, after having deposited most of the lime, flows into a second column C, where the ammonia set free by the lime is distilled off: the spent liquor runs away continuously through *g*, and the gases and vapours pass over by pipe *h* into the first column BA, which serves both for retaining the water and for driving off the volatile ammonium salts contained in the crude gas liquor. The economiser J, and the saturator B, with the gas-bell F, require no special explanation.

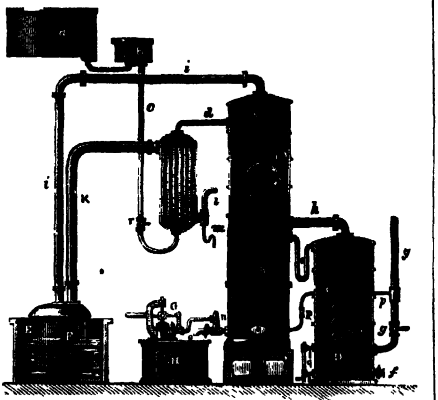


FIG. 2.

In more recent types of still, only a single column is usually employed, the lime being introduced into one of the compartments of the lower portion of the still, which may be made of larger size for this purpose, the hood being also more deeply sealed to effect more vigorous agitation. The mixture of liquor and lime then passes through the lower compartments of the still, constructed in a similar manner to those above. A still of this type, manufactured by the Berlin Anhaltische Maschinen Actien-Gesellschaft is shown in Fig. 3.

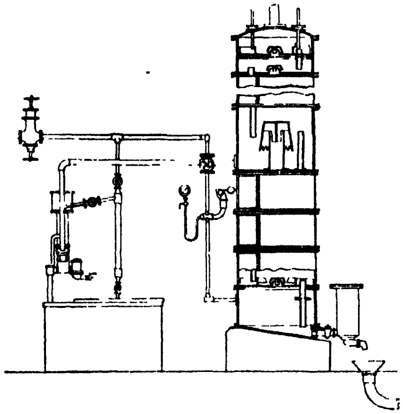


FIG. 3.

Other modifications relate chiefly to improvements in mechanical details, and in making the parts more accessible for cleaning, especially in the portions of the still where lime is present. Thus Wilton (Eng. Pat. 24832, 1901) replaces the central pipe for the steam and circular hood, by a narrow opening extending over nearly the full diameter of the still, and covers this with an inverted trough having serrated edges, which can readily be removed for cleaning from a small manhole at the side. Scott (Eng. Pat. 3987, 1900; 11082, 1901) has patented a process in which the whole of the plant is kept under vacuum, whereby considerable economy of fuel is claimed. The plant and method of working are described by Ballantyne (J. Gas Light. 82, 869).

Absorption of the ammonia in sulphuric acid.—The gases from the still, consisting chiefly of ammonia steam, carbon dioxide, sulphuretted hydrogen, and small quantities of hydrocyanic acid, are conveyed to the saturator (D in Fig. 1, E in Fig. 2) charged with sulphuric acid. This is constructed either of solid lead throughout, or of wood or iron lined with lead, the gases being conducted in by means of a perforated leaden pipe which distributes them over a large area in the saturator and keeps the liquid thoroughly agitated. In some cases, dilute sulphuric acid is used, this being removed and replaced by fresh acid when nearly neutralised. The solution, after settling, is concentrated and crystallised, the mother liquor being returned to the saturator. The dilute solution of ammonium sulphate obtained by direct washing of the crude gas with acid, as in the Mond Gas process, is evaporated and crystallised in a similar way. In most cases, however, when distilling gas liquor, a much stronger acid (of about 140° Tw.) is used which soon becomes saturated, after which the ammonium sulphate crystallises out as formed, and is removed by various means, fresh acid being run in to replace that removed as sulphate. Two types of saturator are employed, (*a*) partly open, (*b*) closed. A common construction of the former type is shown in Fig. 4, the gases entering by the pipe *b* perforated as shown, and bubbling through the acid, the waste gases being led off by the pipe *c*; the sulphate accumulates on the floor of the saturator. The front of the saturator is open, and separated from the closed portion by the sealing curtain *a*, which does not reach to the bottom, and enables the attendant to remove the sulphate periodically by fishing with a perforated ladle, the crystals being placed on a lead-lined drainer fixed so that the mother liquid flows back to the saturator.

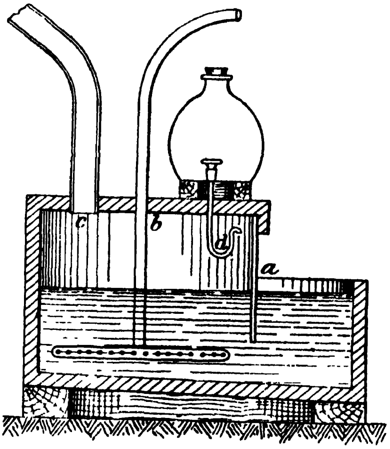


FIG. 4.

When sufficiently dry, the product is placed into stock, or it may be at once dried by a centrifugal machine.

In place of 'fishing,' the sulphate may be periodically or continuously removed from the saturator by means of a steam-ejector, which forces it together with much liquor on to the drainer, thence into a centrifugal machine, the mother liquor in either case returning to the saturator.

With a closed saturator other means of removing the sulphate are adopted, a representative of this type being the Colson saturator, the bottom of which consists of an inverted cone, to the apex of which is fixed a right-angled bend, closed by a simple valve, consisting of a copper disc pressed against the flange of the outlet pipe by a screw clamp. During working this is opened to a sufficient extent to allow the sulphate to fall out almost as soon as it is formed.

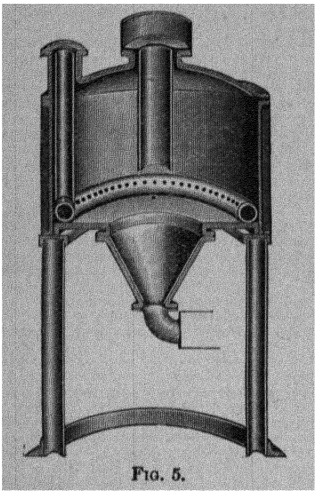


Fig. 5.

The ammonium sulphate thus obtained usually contains from 24 to 25 p.c. of ammonia, equivalent to about 93–99 p.c. of pure ammonium sulphate. It usually contains from 0·1 to 0·5 p.c. of free sulphuric acid, the remainder consisting of moisture and small quantities of insoluble matter. The salt produced with modern plant has mostly a white or greyish-white colour, discolouration by tarry matter being now of rare occurrence with continuous stills, if the liquor is properly separated from tar by settling previous to distillation. When pyrites sulphuric acid is employed, the resulting sulphate may be coloured yellow or brown, by arsenic sulphide, which depreciates its value, and makers therefore prefer to use acid obtained from brimstone or spent oxide. In many cases, however, pyrites acid is used, and the arsenic sulphide which rises as a scum to the surface of the liquid in the saturator removed as it forms, or preferably the acid is previously treated with a portion of the waste gases from the saturator, the sulphuretted hydrogen in which precipitates the arsenic as sulphide, the latter being removed before the acid enters the saturator.

In some cases the sulphate assumes a blue colour on standing in the air, owing to the formation of traces of Prussian blue. From the researches of Forbes Carpenter and Linder (Chief Alkali Inspector's Report, 1905, 51), it appears that this is mostly due to local alkalinity occurring in some portion of the liquid in the saturator, in which case hydrocyanic acid is absorbed at that point, and, with the traces of iron always present, forms ammonium ferrocyanide; the latter, on exposure to the air, oxidises, forming Prussian blue. Priming of the still, resulting in the introduction of ferrocyanides and thiocyanates into the saturator, has a similar effect, but the production of the blue salt often occurs in absence of priming. Its formation is best avoided by maintaining the liquid hot and of sufficient acidity, and arranging that the passage of the gas shall effect a thorough mixing of the liquid in the saturator, so as to prevent the occurrence of local alkalinity.

Waste products in the manufacture of Ammonium Sulphate.—Three waste products are formed in the process: (*a*) the effluent liquor; (*b*) the aqueous condensate from the cooling of the waste gases; (*c*) the waste gases. The effluent liquor is run into settling tanks, where it deposits suspended lime salts, and becomes cooled. The clarified liquor is sometimes run into the sewers, but as it contains large quantities of lime salts (especially thiocyanate and phenols), this is frequently not permitted, and its disposal is often a matter of great difficulty. In gas works it is sometimes got rid of by employing it to quench the hot coke from the retorts, and in some cases it is even evaporated to dryness. Fowler (Alkali Inspector's Report, 1907, 51) allows the liquor, after considerable dilution, to pass through coke filters inoculated with sewage bacteria, which, if gradually accustomed to the liquor, oxidise the thiocyanates and phenols, yielding a fairly pure effluent, and this may be employed for dilution of the fresh liquor going on to the filter. Radcliffe (Eng. Pat. 10075, 1905) removes the thiocyanates by precipitating as cuprous thiocyanate with copper sulphate in presence of sulphurous acid, the latter being obtained by burning a portion of the waste gases. Grossmann (Eng. Pat. 20387, 1905; 7932, 1907; J. Soc. Chem. Ind. 1906, 411) has also described a process for avoiding the production of waste liquor and recovery of the ferrocyanide and thiocyanates present in it.

The avoidance of the production of waste liquor altogether is an especial object in the process of the Otto-Hilgenstock Coke Oven Co. (Eng. Pat. 12809, 1908) now being adopted in some coke-oven works. In this the gas from the ovens is treated for the removal of tar at temperatures above that at which water condenses, and then passed directly through sulphuric acid; the aqueous condensate obtained in the subsequent cooling of the gas is free from ammonia, and only contains small amounts of impurity, and it is claimed that no difficulty is experienced in disposing of it. Wilton (Eng. Pat. 16355, 1909) has patented a somewhat similar process with the same object.

The aqueous condensate obtained by cooling the waste gases is a very noxious-smelling liquid, and is hence termed 'devil-liquor.' It contains sulphuretted hydrogen, pyridines, and similar substances, and hydrocyanic acid, and is also difficult to dispose of. The hot condensate from the liquor-heater or economiser is less objectionable than that obtained in the further cooling of the waste gases, which contains much more sulphuretted hydrogen; but if the latter is returned to the pipe conveying the hot condensate and the waste gases from the economiser, most of the sulphuretted hydrogen is driven off again into the waste gases, and the combined liquor, after cooling, may be mixed with the effluent from the stills without increasing the difficulty of dealing with the latter (Broadberry, J. Gas Light. 69, 345).

The waste gases, after cooling, consist chiefly of carbon dioxide, sulphuretted hydrogen, and smaller quantities of hydrocyanic acid, as well as strongly smelling empyreumatic vapours derived from the tar. With coke-oven liquors, which often contain considerable quantities of cyanide, the amount of hydrocyanic acid may be considerable, necessitating additional care in dealing with it owing to the poisonous nature of the gas. In many cases the gases are burned under the boiler or other furnaces, and discharged with the products of combustion from the chimney; or the gases may be burned separately and the resulting sulphur dioxide absorbed by passing the products through a limestone tower down which water is passing, yielding a solution of calcium bisulphite, or through scrap-iron towers, when a solution of ferrous sulphate is formed (Wilton, Eng. Pat. 15468, 1901). With small and medium-sized plants, the sulphuretted hydrogen and hydrocyanic acid are mostly removed by oxide of iron, in a similar manner to that employed for purifying coal gas. In place of purifying boxes, conical heaps of oxide of iron on a concrete floor are now much used, the gas being introduced from the bottom at the centre of the heap; the spent oxide obtained is saleable for its sulphur content. The sulphuretted hydrogen may also be precipitated with metallic salts, and where sulphuric acid is also made, the gases are burned and passed into the chambers, thus recovering the sulphur as sulphuric acid. A considerable proportion of the waste gas is converted into sulphur by the Claus process (Eng. Pat. 3606, 1882; 5070, 1883; 5958, 1883), also used on the large scale in the Chance sulphur-recovery process. By this method, sufficient air is mixed with the gas to react with the sulphuretted hydrogen in accordance with the equation $2H_2S+O_2=2H_2O+2S$, and the mixture passed through a kiln containing heated ferric oxide, the sulphur formed being deposited in cooling chambers, and the residual gases passed through a small limestone tower and oxide-of-iron purifier to remove any sulphur dioxide or sulphuretted hydrogen remaining. The sulphur obtained is not very pure, owing to tarry matters, &c., present in the gases treated.

Manufacture of Caustic Ammonia (Liquor Ammoniae) and of Liquefied Ammonia.—The pure aqueous solution of ammonia was formerly manufactured by distilling ammonium sulphate with lime in intermittent stills provided with mechanical arrangements for stirring the somewhat thick cream, but it is now usually made by the direct distillation of gas liquor, with suitable purification of the gas evolved from the stills, which is then dissolved in water. In addition to the pure aqueous solution, a crude solution containing sulphide, and sometimes carbonate, is also largely manufactured, this being cheaper and equally applicable to many purposes, especially in the manufacture of soda by the ammonia-soda process, and for the preparation of other ammonium salts. This crude product is termed 'concentrated gas liquor,' two kinds being manufactured, the one containing from 16 to 18 p.c. of ammonia, with both sulphide and carbonate present, and the other from 18 to 26 p.c. of ammonia, with some sulphide but little or no carbonate.

In the manufacture of the first-named liquor, the gases from the stills, worked as in the manufacture of the sulphate, pass through a reflux condenser, to remove some of the steam present, and then through a direct condenser, the gases from which are washed with water. Working in this manner, it is not practicable to obtain a greater strength of ammonia than 16–18 p.c., as with higher concentrations stoppages occur in the condenser from crystallisation of ammonium carbonate.

25 *p.c. Concentrated Liquor.*—In the manufacture of this liquor containing little or no carbonic acid and only small amounts of sulphuretted hydrogen, the crude gas-liquor is first subjected to a preliminary heating to temperatures somewhat below 100° (Hill's process), at which temperature a large proportion of the carbon dioxide and sulphuretted hydrogen are evolved, accompanied by only small quantities of ammonia, the latter being recovered by washing the evolved gases with water or weak ammoniacal liquor, or by other suitable means; the preheated liquor is then distilled as in the case of the sulphate process with the addition of sufficient lime to decompose completely all fixed ammonium salts present, and the steam and gases from the still passed through a reflux condenser, to remove the bulk of the steam, and thence to a condenser; the condensate from the reflux condenser, which contains a considerable amount of ammonia, is returned to the still. The concentrated liquor from the final condenser contains usually about 25 p.c. of ammonia, and has a yellowish colour. It is usually almost free from carbonic acid, and should not contain more than 0·5 p.c. of sulphuretted hydrogen. In addition small amounts of cyanide, ferrocyanide, and thiocyanate are mostly present, derived from the hydrocyanic acid evolved from the crude liquor, and also small amounts of phenols and of pyridine bases.

Pure Caustic Ammonia.—In the manufacture of this product, the procedure in the first part of the process is the same as in the case of the production of the 25 p.c. concentrated liquor To further purify the gases evolved from the still, and to remove as completely as possible all impurities from them after passing the reflux condenser, the gases traverse a set of two or three washers containing cream of lime to remove carbon dioxide, sulphuretted hydrogen, hydrocyanic acid, and phenol vapours, the partly used lime flowing back to the stills to effect the decomposition of the fixed ammonium salts, and recovery of ammonia from the cream. To ensure the removal of the last traces of sulphuretted hydrogen, ferrous sulphate solution is sometimes added to the last lime washer, the ferrous hydroxide formed by the action of the lime retaining the gas as ferrous sulphide, or, according to Pfeiffer (J. Gasbel. 1900, 89), a small final washer containing caustic soda solution is added. Solutions of sodium permanganate or ammonium persulphate may also be used (Foucar). The gases then pass through a series of scrubbers charged with wood charcoal, which remove the strongly smelling empyreumatic substances derived from the tar, and in some cases additional purification in this respect is effected by passing the gas through a fatty or high-boiling mineral oil. The resulting purified gas is then led into distilled water, and thus converted into solution of any desired strength up to about 36 p.c. The charcoal scrubbers must be renewed as soon as their activity becomes lessened, the spent material being revivified by heating in closed retorts.

Technical caustic ammonia is usually clear and colourless, and contains only small quantities of pyridine and empyreumatic substances. When these are present in larger quantity, owing to defective action of the charcoal filters, the liquid assumes a yellowish colour on keeping. Its strength is ascertained from its specific gravity.

Liquefied Ammonia.—The liquefied gas, stored in steel cylinders, is now largely produced and employed for refrigeration purposes. It is manufactured from the gas obtained and purified as described for the manufacture of the pure aqueous solution, but instead of passing t into water, it is well dried, and then compressed by suitable pumping machinery. The commercial liquid usually contains small amounts of water, pyridine, and lubricating oil, and traces of other substances, but is now sold, in many cases, as of guaranteed 99·9 p.c. purity.

Ammonium Chloride (Muriate of Ammonia or Sal-ammoniac).—This salt has been manufactured in a similar manner to that employed or the sulphate, by passing the gases from the stills into hydrochloric acid, but as ead is attacked under these conditions, the saturator must be constructed of stoneware or imilar material, which has many disadvantages. t is now usually made by neutralising hydrohloric acid with concentrated gas liquor, and vaporating and crystallising the resulting olution, or by evaporating a solution of ammonium sulphate and sodium chloride in equivalent proportions; the sodium sulphate formed eparates out during concentration as the monohydrate, which is removed by 'fishing,' eaving finally a concentrated solution of ammonium chloride, which is purified by crystallisaion.

It is also manufactured by neutralising 'galvanisers' pickle" (which consists chiefly of errous chloride) with ammonia, and by the action of ammonium carbonate (or of ammonia and carbon dioxide) on calcium chloride solution, he latter being obtained in large quantity as a by-product in the ammonia-soda manufacture, nd in that of potassium chlorate; the solutions, f ammonium chloride obtained in either case are evaporated and crystallised after removal of he precipitated substances.

Ammonium chloride may be obtained in cubical crystals by adding small amounts of ammonium acetate to the crystallising solution. The modification of crystalline form is probably due to acetamide produced by the decomposition of the ammonium acetate.

Ammonium chloride is frequently purified by sublimation, the sublimed product being known as *sal-ammoniac.* In this country the operation is carried out in large iron pots externally heated and covered with a similar concave iron plate on which the sublimate (sal-ammoniac) forms. This is detached at the end of the operation, the surface adhering to the iron, which is always discoloured, being removed previous to sale. In France the discolouration with iron is avoided by using earthenware pots, but the product is more expensive, owing to the fact that the pots are destroyed at each operation.

The commercial crystallised salt is white or only slightly discoloured, whilst the sublimed material has a fibrous structure, and frequently contains small amounts of iron. It is employed in pharmacy, soldering, galvanising, dyeing, and calico-printing, and in small quantities for many other purposes.

Ammonium Carbonate (Sal-Volatile).—The commercial product sold under this name consists of a mixture of ammonium bicarbonate $NH_4 \cdot HCO_3$ with ammonium carbamate $NH_2 \cdot CO \cdot ONH_4$, and contains about 31 p.c. of ammonia and 56 p.c. of carbon dioxide. It is usually prepared by subliming a mixture of about 1 part of ammonium sulphate with 1·5 to 2 parts of chalk in retorts, the evolved gases being passed into leaden chambers, where the carbonate is deposited as crusts on the walls, the exit gases being washed with water or sulphuric acid to recover the uncondensed ammonia. Lunge recommends the passing of an additional quantity of carbon dioxide through the chambers to effect a more complete recovery of the ammonia. As soon as the crust has attained a sufficient thickness it is detached, and is usually purified by resublimation. In Kunheim's process, the carbonate is prepared by passing ammonia obtained by the distillation of gas liquor direct into chambers, where it mixes with carbon dioxide and deposits the carbonate as a crust. (*See also* Bueb, Eng. Pat. 9177, 1910.)

The commercial product forms crystalline crusts, smelling strongly of ammonia, which is partially evolved on exposure to the air, the mass efflorescing and leaving a powder consisting of ammonium bicarbonate. It is employed in wool-scouring, dyeing, and as a constituent of baking powders.

Ammonium Nitrate.—This salt is produced to a very large extent for use in the explosive industry and in the preparation of nitrous oxide. It may be obtained by neutralising caustic ammonia with nitric acid, and evaporating and crystallising the solution if necessary, or by passing ammonia-gas from the stills, after purification, into commercial nitric acid, the heat evolved by the combination causing the evaporation of the water present and production of fused ammonium nitrate. Calcium nitrate may also be converted into ammonium nitrate by passing ammonia and carbon dioxide through its aqueous solution, calcium carbonate being precipitated. It is, however, now chiefly prepared from ammonium sulphate and sodium nitrate by the process of Freeth and Cocksedge (Eng. Pat. 120678). This process depends on the fact that when a solution saturated with respect to ammonium nitrate, sodium nitrate and sodium sulphate at any given temperature, but not in contact with the solid salts, is diluted with sufficient water to enable the sodium salts to be retained in solution at a lower temperature to which it is to be cooled on dilution, then, on cooling to that temperature ammonium nitrate crystallises out in practically pure condition. After separation of the nitrate, the clear solution is concentrated to drive off the amount of water added on previous dilution, and a further quantity of a mixture of equivalent amounts of sodium nitrate and ammonium sulphate added. The whole is maintained at a temperature not lower than that at which the original was saturated previous to dilution with water. Sodium sulphate then separates in practically pure condition, and after its removal the dilution with water and cooling is repeated, and the cycle of operations repeated. In this manner the whole of the ammonium sulphate and sodium nitrate are completely converted into practically pure ammonium nitrate and sodium sulphate.

Calcium nitrate may also be converted into the ammonium salt by passing ammonia and carbon dioxide gases through its aqueous solutions, calcium carbonate being precipitated.

Ammonium phosphate. Monammonium phosphate $(NH_4)H_2PO_4$, and diammonium phosphate $(NH_4)_2HPO_4$ have become commercial products by the process of Lagrange, which starts from commercial calcium superphosphate. This is lixiviated by water and steam, and a solution of 42°Tw. is obtained, together with a residue of calcium sulphate. Some of the latter remains in the solution, and is removed by carefully adding barium carbonate. The filtrate is neutralised by ammonia in slight excess, whereby all the lime is precipitated as basic phosphate, which is washed and used over again for the manufacture of superphosphate. The filtered solution, marking 32°Tw., contains monammonium phosphate, and can be worked for this or for diammonium phosphate. The latter is obtained by gradually mixing the above solution with *liquor ammoniæ* of sp.gr. 0·92, in the proportion of 1¼ equivalents of NH_3 to 1 of $(NH_4)H_2(PO_4)$. The diammonium phosphate at once separates out as a crystalline mass, which, after cooling, is submitted to hydraulic pressure. The operation is carried out in a closed vessel, to prevent the escape of ammonia. The mother liquor is employed for the manufacture of ammonia. The diammonium phosphate is principally used in Lagrange's sugar-refining process.

Ammonium thiocyanate is manufactured in considerable quantity in the crude state, but the product is for the most part simply employed as an intermediate product in the manufacture of cyanides. It occurs, as has been mentioned, in considerable amount in gas-liquor, and also in spent oxide, from which it may be extracted by water, but in both cases it is mixed with so many other impurities that its recovery is not remunerative; it may, however, be easily isolated as cuprous thiocyanate by precipitation with copper sulphate and sulphurous acid. It is prepared synthetically from carbon disulphide by absorbing the latter in ammonia in presence of bases such as lime (Albright and Hood, Eng. Pat. 14154, 1894), the ammonium thiocarbonate first produced undergoing conversion into thiocyanate. A concentrated solution of ammonium thiocyanate is now prepared in a number of gas works, according to the British Cyanide Co.'s and Williams' process (Eng. Pat. 13653, 1901), by passing the crude gas containing ammonia and hydrocyanic acid through a purifier containing sulphur in the form of spent oxide and moistened with water and fed with powdered sulphur, the ammonium polysulphide first formed combining with the hydrocyanic acid to form thiocyanate, solutions of 30–50 p.c. strength being readily obtained, which only contain small amounts of other non-volatile ammonium salts.

The pure salt is used in dyeing and calico-printing, and may be obtained from the crude product by first converting it into the barium salt with baryta-water; or the barium salt may be produced by the action of barium sulphide on cuprous thiocyanate. After purification by recrystallisation, the barium salt is exactly precipitated with ammonium sulphate, and the solution evaporated and crystallised. The white deliquescent salt has frequently a reddish colour, due to the formation of the red ferric thiocyanate, from traces of iron present.

Ammonium persulphate. This salt is now produced on the commercial scale by the electrolysis of ammonium sulphate, and is employed for photographic purposes and as an oxidising agent. The commercial product usually contains small quantities of lead derived from the electrodes used in its manufacture.

H. G. C.

AMMONIACUM, AFRICAN, GUM, PERSIAN, *v.* Gum Resins.

AMMONITE *v.* Explosives.

AMMONIUM MELEQUETA *v.* Cocculus Indicus.

AMPANGABEITE. A rare-earth mineral from Madagascar, described by A. Lacroix in 1912. It is a tantalo-columbate (containing but little titanium) of uranium (UO_3 19·4 p.c.), iron, yttrium, thorium, &c. The crystals are orthorhombic and form sub-parallel groupings of large prisms of a brown colour and bright greasy lustre. Sp.gr. 3·97–4·29, depending on the degree of hydration, the material being optically isotropic. The mineral occurs associated with beryl, columbite, strüverite, and monazite in pegmatite veins at Ampangabe, Ambatofotsikely, and Tongafeno. A considerable number of loose crystals have been collected from the weathered debris of the pegmatite.

L. J. S.

AMPELOPSIDIN, AMPELOPSIN, *v.* Anthocyanins.

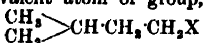
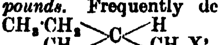
AMPHOTROPHIN. Trade name for hexamethylenetetramine camphorate.

AMRAD-GUM. This gum forms white, yellow, and brown lumps of a sweetish taste and resinous smell. An aqueous solution (1 : 2) is viscid and strongly adhesive. It also gives with oil excellent emulsions, which keep very well. The dry substance contains 5·61 p.c. of ash, consisting of carbonic acid, lime, iron, magnesia, traces of phosphoric acid and silica. Has been recommended as a substitute for gum arabic. It was brought into the market some years ago, and comes from the Abyssinian highlands; is probably obtained from *Acacia etbacia* (Schweinfurth). (H. Unger and Kempf. Pharm. Zeit. 33, 218; J. Soc. Chem. Ind. vii. 446.)

AMYGDALASE, AMYGDALIN *v.* GLUCOSIDES.

AMYGDONITRILE GLUCOSIDE *v.* GLUCOSIDES.

AMYGDOPHENIN *v.* SYNTHETIC DRUGS.

AMYL signifies the hypothetical monovalent radical $C_5H_{11}—$, derived from the three isomeric pentanes, C_5H_{12}, by removal of one hydrogen atom. Normal pentane may have one hydrogen atom substituted by a monovalent atom or group in three ways, secondary pentane or dimethylethylmethane may have one hydrogen atom substituted in four ways, and tertiary pentane or tetramethylmethane may have one hydrogen atom substituted in one way. There are thus eight series of derivatives of the radical 'amyl.' It is usual to designate as *amyl compounds* those of the type $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2X$, where X signifies a monovalent atom or group, and those of the type  $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH{\cdot}CH_2{\cdot}CH_2X$ as *isoamyl compounds*. Frequently derivatives of the type  $\begin{matrix}CH_3{\cdot}CH_2\\CH_3\end{matrix}\!\!>C<\!\!\begin{matrix}H\\CH_2X\end{matrix}$, when in the optically active form, are referred to as *active amyl compounds*, as the commonly occurring active amyl alcohol belongs to this class. The other types of amyl derivatives are designated according to the usual methods of nomenclature in organic chemistry.

The amyl compounds of technical importance are all prepared from fusel oil, and are therefore in no case pure chemical individuals, but consist of an *iso*amyl compound containing a variable proportion of the corresponding *d*-amyl derivative.

Amyl Alcohols $C_5H_{11}OH$. The eight theoretically possible structural isomerides are all known. Of these, three should also be capable of existing as optically active stereoisomerides. This has been realised in two cases, but not in the third, namely that of methyl*iso*propylcarbinol.

n-**Amyl Alcohol** $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH$ (Pentanol). This alcohol was prepared in an impure state by Schorlemmer (Annalen, 1872, 161, 269) from crude pentane. Wischnegradsky (Annalen, 1878, 190, 328) concluded that it was present in commercial amyl alcohol, but this has been shown to be incorrect (Tissier, Bull. Soc. chim. [3] 9, 100).

It is a colourless liquid of fusel oil odour; b.p. 137·7°; $D^{20°}_{20°}=0·8168$. It is best prepared by reducing valeramide with sodium and alcohol (Chem. Zentr. 1904 [2] 1698), or by a similar reduction of ethyl-*n*-valerate or ethyl-*n*-propylacetoacetate (D. R. P. 164294, 1905; *see* also Biochem. Zeitsch. 1914, 62, 470; and Annalen, 159, 70; 233, 253).

Isobutyl Carbinol $(CH_3)_2CH{\cdot}CH_2CH_2OH$ (3-methylbutanol). Ordinary *iso*amyl alcohol, fermentation amyl alcohol, is the chief constituent of most fusel oils. It also occurs as angelic and tiglic esters in oil of camomile (Annalen, 195, 99). It constitutes from 50 to 85 p.c. of technical amyl alcohol. (For further details as to the isolation of *iso*amyl alcohol from fusel oil, &c., *see* below under 'Fusel Oil.')

It is a colourless liquid possessing a characteristic, cough-provoking, odour; b.p. 131·4°/760 mm., 46·8°/14·2 mm. It freezes at −134°, and melts at −117·2°; $D^{0°}_{4°}=0·823$. It is soluble in 50 parts of water at 13·5°. One litre of water dissolves 34·7 c.c. isoamyl alcohol; 1 litre of the alcohol dissolves 22·14 c.c. water.

It may be prepared synthetically by reducing *iso*valeric acid (from *iso*butylalcohol), or better, by the action of trioxymethylene on *iso*butylmagnesium bromide (Locquin, Bull. Soc. chim. 1904, [3] 31, 599). It is a strong poison both to human beings and to bacteria. It is about eight times as poisonous to man as ethyl alcohol.

Derivatives.—Urethane, m.p. 64·5°; phenyl urethane, m.p. 54°; phenyl carbamate, m.p. 55°.

Secondary Butyl Carbinol

$CH_3{\cdot}CH_2CH(CH_3){\cdot}CH_2OH$

(2-methylbutanol). Active amyl alcohol, the second constituent of commercial amyl alcohol, is a colourless liquid of similar odour to the above. The vapour does not provoke coughing, but has greater stupefying effects; b.p. 128°; $D^{20°}_{4°}=0·816$; $[a]^{20°}_{D}=-5·90°$.

The active alcohol, in spite of its lævorotation is more correctly termed *d*-amyl alcohol, on account of its genetic relationships with *d*-*iso*leucine and with *d*-valeric acid. The oxidation of the alcohol yields pure *d*-methylethylacetic acid. For the methods of isolating the pure active alcohol from fusel oil, *see* below, under 'Fusel Oil.' It should be noticed that all technical amyl compounds contain variable amounts of the active amyl derivatives.

Derivatives.—Urethane, m.p. 61°; phenyl carbamate, m.p. 30°; 3-nitrophthalate, m.p. 114°.

The active alcohol is partially or wholly racemised by heating above 200°, more especially when in the form of sodium amylate or in the presence of salts soluble in the liquid (Chem. Soc. Trans. 1897, 71, 256; Proc. Roy. Soc. 17, 308). The racemic alcohol has been synthesised by the reduction of natural or synthetic tiglic aldehyde (Herzig, Monatsh. 3, 122), and by the action of secondary butylmagnesium bromide on trioxymethylene (Freundler and Damond, Bull. Soc. chim. [3] 35, 110). It has b.p. 128°/749 mm. Its acid *m*-nitrophthalate melts at 117°. A mixture of racemic with *l*-amyl alcohol was obtained by Le Bel (Bull. Soc. chim. 1878, [2] 31, 104).

Tertiary Butylcarbinol $(CH_3)_3C{\cdot}CH_2OH$ (2·2-dimethylpropanol). This alcohol is a volatile solid melting at 52°–53°, and has a pleasant turpentine-like odour; b.p. 113°–114°. It has all the characteristic properties of a primary alcohol.

It has been prepared by reduction of trimethylacetyl chloride, also, in poor yields, by chlorination, &c., of tetramethylmethane and by the action of a Grignard reagent on paraformaldehyde or methyl formate (Tissier, Ann. Chim. Phys. [6] 29, 340; Samec, Annalen, 351, 256; Bouveault, Compt. rend. 138, 985, 1108).

The action of nitrous acid upon this alcohol yields not this alcohol, but the isomeric dimethylethylcarbinol (Tissier, Compt. rend. 112, 1065).

Methyl-*n*-propylcarbinol $CH_3{\cdot}CH(OH){\cdot}C_3H_7$ (pentanol-2). This is a colourless liquid of b.p. 119°, and $D_{20°}^{20°}=0{\cdot}8102$. It is prepared by the reduction of methyl-*n*-propyl ketone by means of sodium amalgam, or better, by the method of Sabatier and Senderens (Chem. Zentr. 1903, [2] 708). The best method of preparation is by the action of propylmagnesiumbromide on acetaldehyde.

This alcohol is racemic. Le Bel, using *Penicillium glaucum*, obtained a lævorotatory specimen (Compt. rend. 89, 312). Pickard and Kenyon (Chem. Soc. Trans. 1911, 99, 45), by crystallisation of the strychnine and brucine hydrogen phthalates, obtained the pure *d*-alcohol; b.p. 118·5°–119·5°; $D_{4°}^{12{\cdot}3°}=0{\cdot}8169$; $[\alpha]_D^{20°}=+13{\cdot}70°$.

Methylisopropylcarbinol

$CH_3{\cdot}CH(OH){\cdot}CH(CH_3)_2$

(4-methylbutanol-2), a colourless liquid of b.p. 113°, which has the fusel oil odour. It does not freeze at −33°. It has $D_{19°}^{19°}=0{\cdot}819$. Hydrogen halides react with it very slowly to produce only tertiary compounds, such as $C_2H_5{\cdot}(CH_3)_2{\cdot}C{\cdot}Cl$. It has been prepared by the reduction of the corresponding ketone, and, in good yield, by the peculiar action of zinc dimethyl upon bromoacetyl bromide or chloroacetyl chloride (Annalen, 191, 127; 209, 87). It may also be obtained by the interaction of methylmagnesium bromide and isobutylene oxide, chloroacetone, or chloroacetyl chloride (Compt. rend. 145, 21).

This alcohol is racemic; the optically active components have not been isolated.

Diethylcarbinol $C_2H_5{\cdot}CH(OH){\cdot}C_2H_5X$ (pentanol-3). This is a colourless liquid having the usual amyl alcohol odour; b.p. 114°–115°/749 mm.; $D^{14{\cdot}7°}=0{\cdot}8271$.

It is prepared by the action of ethyl formate on zinc ethyl (Annalen, 175, 351), or on ethylmagnesiumbromide (Chem. Zentr. 1901, [2] 623).

Derivative.—Phenyl urethane, m.p. 48°–49°.

Ethyldimethylcarbinol $C_2H_5{\cdot}C(CH_3)_2OH$ (1-1-dimethylpropanol). This alcohol, commonly known as 'amylene hydrate,' is a colourless liquid possessing an odour resembling that of camphor; b.p. 101·5°–102°; m.p. −12°; $D_{15°}^{15°}=0{\cdot}8144$.

It has been prepared synthetically by the interaction of propionyl chloride and zinc dimethyl (Annalen, 190, 328). It is produced commercially by treating amylene with aqueous sulphuric acid, and subsequently boiling the solution. Trimethylethylene, the chief constituent of commercial amylene, is thus quantitatively converted into tertiary amyl alcohol, which is employed medicinally as a hypnotic.

Fusel Oil is the source of all commercial amyl compounds. It is a yellow or brownish liquid possessing a nauseating taste and a characteristic unpleasant, cough-provoking odour. It boils from 80° upwards, but chiefly between 128° and 132°. It has a density of about 0·83. It burns with a bright flame, and its main constituents are usually *iso*amyl alcohol and active (lævorotatory) *d*-amyl alcohol in varying proportions.

The larger quantity of commercial fusel oil is obtained as a residue in the refining of the crude spirit from the fermentation of potatoes or molasses. The separation is effected by fractionating the fermented liquor, usually in a continuously operating plant (*see* under ALCOHOL). When the ethyl alcohol content of the liquid has fallen to 15 p.c. the fusel oil may be removed from the surface, where it separates as an oily layer. Crude spirit after fractionation may contain 95 p.c. of ethyl alcohol, and usually about 0·4 p.c. of fusel oil. Brandy contains at the most only traces, but the spirits having the most pleasing aroma, those from corn or fruit, *e.g.* cherries, &c., may contain up to 0·6 p.c. or more of fusel oil, partly in the form of esters The presence of the fusel oil may increase the intoxicating qualities of the spirit, but the harmful effects of excessive spirit drinking seem to be mainly caused by ethyl alcohol.

The chief constituent of most fusel oils is the mixture of amyl alcohols which constitutes 65–80 p.c. of the whole, and which is sold as commercial amyl alcohol of b.p. 128°–132°. The proportions in which the two amyl alcohols occur in commercial amyl alcohol vary considerably, as Marckwald pointed out, according to the source of the specimen. Ordinary corn or potato amyl alcohol contains from 13·5 to 22 p.c. of the active isomeride, while the amyl alcohol from molasses fusel oil contains from 48 to 58 p.c. of the lævorotatory alcohol. Besides the amyl alcohols, ordinary fusel oils contain usually from 15 to 25 p.c. of *iso*butyl alcohol (b.p. 108°), and from 4 to 7 p.c. of *n*-propyl alcohol (b.p. 97°). But the fusel oils from wines may contain large quantities (as much as 50 p.c. of the whole) of *n*-butyl alcohol. That produced by the Fernbach Fermentation Process is said to contain 65 p.c. of butyl alcohol.

In addition to these main constituents, there are always present in small quantities some or all of the following: hexyl and heptyl alcohols, furfurol, acetaldehyde, *iso*butyl and valeric aldehydes, ammonia and amines, pyridine, pyrazine derivatives, traces of all the fatty acids up to capric acid in the form of ethyl, amyl or oenanthyl esters, terpene and terpene hydrate.

The formation of fusel oil in fermentation has been explained by Ehrlich (Ber. 1906, 39, 4072; 1907, 40, 1027, 2538; 1912, 45, 1006; Biochem. Zeitsch. 1911, 36, 477; *see* also Biochem. Zeitsch. 1907, 3, 121; 1908, 10, 490). Ehrlich has shown that the addition of leucine and *d*-*iso*leucine, in the form of, *e.g.*, hydrolysed egg albumen, during the fermentation process, results in a largely increased yield of amyl alcohols. This is made the basis of a technical method (D. R. P. 177174). Leucine, from egg albumen, can also be converted by dry distillation into amylamine (D. R. P. 193166), and thence into a mixture of amyl alcohols similar to that occurring in fusel oil.

Detection and Estimation.—Fusel oil is best detected in spirits by rubbing a little of the liquid between the hands, when the ethyl alcohol evaporates and the residue reveals itself by its smell. When a large quantity is available for the estimation, it may be accomplished by subjecting the material to fractional distillation. For ordinary purposes the usual method depends on the extraction of the fusel oil from a 30 p.c. ethyl alcohol solution by means of chloroform, the increase in volume of the latter being observed (*see* Ehrlich, Ber. 1907, 40, 1031; Pringsheim, Biochem. Zeitsch. 1907, 3, 233). For another valuable method, *see* Aberhalden's Handbuch der biochemische Arbeitsmethode, ii. 11; *v.* FUSEL OIL.

Uses.—Fusel oil and commercial amyl alcohol are valuable solvents for resins, fats, and oils; amyl alcohol, being much more useful for these purposes than ethyl alcohol, is therefore indispensable in industry. It is much used in the nitrocellulose smokeless powder and lacquer industries. It has been proposed as a raw material for the production of synthetic rubber (Perkin, J. Soc. Chem. Ind. 1912, 31, 616).

Preparation of Isoamyl and d-Amyl Alcohol from Fusel Oil.—This separation was first partially effected by Pasteur (Annalen, 1855, 96, 255) by the fractional crystallisation of the barium salts of the amyl sulphuric acids. Le Bel went further, using the fact that conversion of the alcohols into the chlorides by hydrogen chloride left a more active residue than the original mixture (Bull. Soc. chim. [2] 21, 542; 25, 545). Marckwald finally isolated the two alcohols in a state of chemical purity (Ber. 1901, 34, 479, 485; 1902, 35, 1595, 1602; 1904, 37, 1038), by fractional crystallisation of the 3-nitrophthalic esters and also by using Pasteur's method. All the pairs of derivatives of the two components of natural amyl alcohol examined by Marckwald formed mixed crystals.

To obtain *iso*amyl alcohol, use a potato amyl alcohol containing 80 p.c. of *iso*amyl alcohol and convert it at once into the 3-nitrophthalic ester, which is quickly purified by recrystallisation.

To obtain *d*-amyl alcohol (lævorotatory), use the molasses amyl alcohol containing at least 50 p.c. of the required compound. Saturate with dry hydrogen chloride at 0°, and heat in an autoclave for five hours at 110°. On distillation of the product a liquid is obtained containing 80 p.c. of the active alcohol. This is then converted into the 3-nitrophthalate and recrystallised from benzene until the melting-point of the compound is 114°. The two alcohols are very easily obtained from the acid nitrophthalic esters by hydrolysis.

Amyl Acetate $C_5H_{11}O{\cdot}CO{\cdot}CH_3$. A colourless neutral mobile liquid having a penetrating odour resembling that of jargonelle pears; b.p. 138·5°–139°; $D^{15°}_{4°} = 0{\cdot}875$. Is easily inflammable, and sparingly soluble in water, but easily so in organic solvents. For its preparation, 1 part of commercially pure amyl alcohol, 1 part of glacial acetic acid, and ½ part of concentrated sulphuric acid, are heated at 100° for five hours, the mixture poured into water and the oil separated. The oil is shaken with a strong aqueous solution of sodium carbonate, dried, and distilled. (*See* also Compt. rend. 1911, 152, 1671; and Eng. Pat. 4669, where fusel oil, hydrochloric acid, and calcium acetate are used.)

The alcoholic solution is largely used under the name of 'Jargonelle Pear Essence,' for flavouring confectionery. Amyl acetate is an excellent solvent for gun-cotton, camphor, tannin, and resins, and is therefore greatly used in the celluloid and varnish industries. It is also used in the manufacture of smokeless powder and photographic films. It is recommended as a standard oil in photometry (J. Soc. Chem. Ind. 1885, 262). *See also* ACETIC ACID.

Amyl Ether $C_5H_{11}{\cdot}O{\cdot}C_5H_{11}$. A colourless liquid possessing a pleasant pear-like smell; b.p. 172·5°–173°; $D15° = 0{\cdot}7807$. It is prepared by heating the alcohol to its boiling-point with 1/10 part of concentrated sulphuric acid (D. R. P. 200150), or with 1/10 part of amyl iodide in an autoclave at 250°. It is used as a solvent in the Grignard reaction, for fat extraction, for perfumes, alkaloids, in the varnish industry, and therapeutically.

Amyl Formate $C_5H_{11}O{\cdot}CO{\cdot}H$. A fragrant liquid of b.p. 123·3°; and $D^{0°}_{4°} = 0{\cdot}8944$, prepared from fusel oil and formic acid or from fusel oil, glycerol, and oxalic acid. It is used in the synthetic fruit essence industry and in the laboratory in the preparation of oxymethylene derivatives.

***d*-Amyl Mercaptan** $C_5H_{11}{\cdot}SH$. A liquid of b.p. 119°–121°, was prepared in a state of purity from fusel oil by Vorocek and Vesely (Ber. 1914, 47, 1515) and used to resolve racemic arabinose into its optically active components.

Amyl Nitrite $C_5H_{11}O{\cdot}NO$. A yellow neutral, or feebly acid liquid, possessing a fruity smell; b.p. 97°–99°; $D15° = 0{\cdot}870–0{\cdot}880$. It burns with a brilliant flame. It should be kept protected from light, but in any case it is best either freshly prepared or repeatedly fractionated before use. The vapour should not be inhaled. It is prepared by passing nitrous fumes into amyl alcohol kept at 70°–90° (Balard, Ann. Chim. Phys. [3] 12, 318; Williams and Smith, Pharm. J. 1886, 499). Bouveault and Wahl passed nitrosyl chloride into a dry mixture of pyridine and amyl alcohol (Compt. rend. 136, 1563). For a rapid method of preparation, involving sodium nitrite, *see* Ber. 1886, 19, 915.

The pure isoamyl nitrite has b.p. 97° and $D\,15° = 0{\cdot}880$ (Dunstan and Williams, Pharm. J. 1889, 487).

It is used in the preparation of diazo and *iso*nitroso compounds or nitroso chlorides, and as the 'amylium nitrosum' of medicine for the treatment of epilepsy, asthma, angina pectoris, &c., since it reduces blood pressure and retards the pulse. It is also used in the manufacture of sweets, perfumes, fruit essences, &c., in spite of its harmful effects.

Tertiary amyl nitrite $(CH_3)_2(C_2H_5){\cdot}C{\cdot}O{\cdot}NO$ (Bertoni's 'Amylonitrous Ether') has been used as a substitute for ordinary amyl nitrite, its action being stronger in degree and more lasting. It is a yellow liquid of weak camphoraceous odour and peppermint taste; b.p. 93° (J. Soc. Chem. Ind. 1889, 1003).

Amyl Salicylate $C_5H_{11}O{\cdot}CO{\cdot}C_6H_4{\cdot}OH$ (Amylenol) is a colourless refractive liquid of b.p. 250° (with decomposition), and 115°/2 mm.; $D\,15° = 1{\cdot}065$. It is produced by passing dry hydrogen chloride into a saturated solution of salicylic acid in amyl alcohol, and after some hours pouring into water and working up as usual.

It is used medicinally as an antirheumatic and in the perfume and fruit essence industry C. S. G.

AMYLACETIC ACID (Active) *v.* HEPTOIC ACIDS.

iso-**AMYLACETIC ACID** *v.* HEPTOIC ACIDS.

α- and *β*-**AMYLANS** $n(C_6H_{10}O_5)$?

After first extracting cereals with strong alcohol, the aqueous extract contains gummy lævorotatory colloidal carbohydrates, which are precipitated by strong alcohol. The product so obtained from barley is a mixture, part being soluble in cold water. The insoluble crumbly residue, amounting to 2 p.c. of the barley, is *α*-amylan. It has $[\alpha]_D - 21{\cdot}6$, and does not reduce Fehling's solution; it is gelatinised in hot water, and yields viscous solutions even at 1–2 p.c. concentration. O'Sullivan (Chem. Soc. Trans. 1882, 41, 24) found it to be present in barley, oats, wheat, and rye, especially in the two first named. The soluble product *β*-amylan has $[\alpha]_D - 65°$; it amounts to 0·3 p.c., and is very similar to *α*-amylan in properties.

O'Sullivan obtained from *β*-amylan, by fractional precipitation with alcohol or on boiling with milk of lime, a similar substance $[\alpha]_D - 129{\cdot}7°$. This he regarded as a decomposition product, but this is probably not the case. O'Sullivan states that the amylans yield glucose alone on hydrolysis. Lintner and Düll (Zeit. angew. Chem. 1891, 538) obtained galactose and xylose from barley gum. Wroblewski (Ber. 1893, 30, 2289) obtained arabinose. Lindet (Berlin Congress, 1903, 3, 498) isolated a dextrorotatory gum from barley, in addition to a lævo-rotatory gum.

Contrary to O'Sullivan's statement that diastase is without action on amylan, Horace Brown (Trans. Guinness Research Laboratory, 1906, 317, where there is a full account of amylan) finds that when barley gum is steeped in malt extract it swells up and undergoes gradual liquefaction and solution, and in a few days its colloidal nature is lost. This is one of the most significant changes which mark the conversion of barley into malt.

To prepare 'amylans' in quantity, Brown boils the finely divided grain with water, treats with malt extract at 50°–55° for an hour to liquefy the starch, boils again, and filters. The filtrate is concentrated in vacuum to sp.gr. 1·060, and three volumes 80 p.c. alcohol (by volume) added gradually. The crude amylans are precipitated in large white flocks free from dextrin and have no cupric reducing power. Corrected for ash and nitrogen they amount on a number of dry barleys to about 9·6 p.c., and have $[\alpha]_D + 62°$ to $+73°$. This amount practically accounts for the whole of the missing constituents of the soluble portion of barley after hydrolysis with malt extract.

On hydrolysis about 60 p.c. of glucose is formed, together with arabinose, xylose, and an unknown substance of low angle and reducing power.

The above dextrorotatory amylan represents everything insoluble in 62 p.c. alcohol. By a variation of the method of preparation a carbohydrate $[\alpha]_D - 100{\cdot}34°$, corresponding to Wroblewski's araban, was obtained.

It is obvious that the 'amylans' require further investigation. According to O'Sullivan, it is probably owing to the presence of amylan that unmalted barley cannot be satisfactorily employed in the preparation of beer. Malted grain does not contain it. Distillers using raw grain (oats and barley) have at times much difficulty in separating the wort (solution of sugars, &c.) from the grains (undissolved portion of the grain employed) in consequence of the presence of amylan in quantity, the barleys and oats of some seasons containing much more of it than at other times. E. F. A.

AMYLARINE. *Iso*amyltrimethylammonium hydroxide.

AMYLASE *v.* DIASTASE; *also* ENZYMES.

AMYLENE C_5H_{10}. Eight isomeric amylenes are theoretically possible, and all have been prepared. These hydrocarbons have been chiefly studied by Flavitzky (Annalen, 179, 340), Wyschnegradsky (Annalen, 190, 336), and by Kondakoff (J. Russ. Phys. Chem. Soc. 24, 381), and can be obtained by the action of alcoholic potash on the various amyl iodides; or by the action of dehydrating agents such as sulphuric acid or zinc chloride on amyl alcohol. They can often be converted into one another by the action of hydriodic acid and the subsequent removal of the latter, thus:

$$\mathrm{Me_2CH\,CH:CH_2+HI}$$
$$\longrightarrow \mathrm{Me_2CH\,CHIMe} \xrightarrow[\text{+alcohol}]{\text{KOH}} \mathrm{Me_2C:CHMe}$$

The amylene ordinarily met with is trimethylethylene, and is chiefly obtained by the dehydrating action of zinc chloride on fermentation amyl alcohol.

Preparation.—To prepare amylene, fermentation amyl alcohol (1 part) is shaken with coarsely powdered zinc chloride (1½ parts), allowed to remain for twenty-four hours, and then distilled. The product consists of a complex mixture of paraffins from C_5H_{12} to $C_{10}H_{22}$ with olefines from C_5H_{10} to $C_{10}H_{20}$ (Wurtz, J. 1863, 507). These can be isolated by fractional distillation (Wurtz), but according to Eltekow (J. Russ. Chem. Soc. 14, 379), amylene is most readily obtained if the product is well cooled, and shaken with dilute sulphuric acid (2 vols. of acid to 1 vol. of water), the acid layer separated, diluted with water, and distilled; the distillate consists of amylene (trimethylethylene) and tertiary amyl alcohol, and the latter, on distillation with sulphuric acid (1 : 1), yields pure trimethylethylene. Amylene may be satisfactorily obtained from commercial amyl alcohol under the following conditions: Amyl alcohol (1·5 litres) and concentrated sulphuric acid (100 c.c.) are heated to vigorous boiling under a reflux condenser in which the water is maintained at such a temperature (60°–90°) as to allow a considerable amount of vapour to distil out of the apparatus; the top of the condenser is connected with a second, efficiently cooled condenser, attached so as to permit downward distillation. The heating requires a maximum time of about eight hours. At first, water and amyl alcohol pass over, whilst subsequently amylene distils. The distillate is washed with sodium hydroxide to remove sulphur dioxide and the amylene isolated by fractionation. It appears to consist of *β*-methyl-Δ*α*-butylene and

β-methyl-Δ^{β}-butylene containing only a negligible amount of γ-methyl-Δ^{α}-butylene. The residue in the original flask contains amyl alcohol and *iso*amyl ether, which are recovered by distillation with steam and subsequent fractionation. About 250 c.c. of amylene 400 c.c. of *iso*amyl ether, and 500 c.c. of amyl alcohol are obtained from 1500 c.c. of the latter (Adams, Kamm, and Marvel, J. Amer. Chem. Soc. 1918, 40, 1950; Chem. Soc. Abstr. 1919, i. 61). Larger amounts of amylene are more conveniently obtained by the pyrogenic-catalytic method, using aluminium oxide as catalyst at 500°–540°, using a suitably electrically heated furnace (*cf.* Ipatieff, Abst. 1903, i. 593). The yield of amylene is 70–80 p.c. of the theoretical, and the product is about 98–99 p.c. pentene. The catalyst retains its activity for a long time. Pure trimethylethylene can be prepared by heating tertiary amyl iodide Me_2CIEt with alcoholic potash (J. Russ. Phys. Chem. Soc. 17, 294). It can also be formed by dropping tertiary amyl alcohol on to oxalic acid (D. R. P. 66866).

Other methods for obtaining ordinary amylene have been described by Balard (Ann. Chim. Phys. [3] 12, 320); Bauer (J. 1861, 659), and Linnemann (Annalen, 143, 350); Kondakoff (*l.c.*); Ipatieff (J. Russ. Phys. Chem. Soc. 30, 292); Tornöe (Ber. 21, 1282); Blaise and Courlot (Bull. Soc. chim. 35, 582).

Properties.—Amylene is a colourless liquid, b.p. 36°–38° and sp.gr. 0·6783 at 0° (Le Bel, Bull. Soc. chim. 25, 547); b.p. 36·8° at 752·7 mm. (Schiff, Annalen, 223, 65). It combines directly with a large number of substances: with nitric peroxide (Guthrie, Chem. Soc. Trans. 13, 129; Wallach, Annalen, 241, 291; 248, 161; Miller, Chem. Soc. Proc. 3, 108; Demganoff, Chem. Zentr. 1899, i. 1064); sulphur chloride and chlorine (Guthrie, Chem. Soc. Trans. 12, 112; 13, 45, 129; 14, 136; Kondakoff, J. Russ. Phys. Chem. Soc. 20, 141; 24, 381; Ber. 24, 929; Hell and Wildermann, *ibid.* 216); with bromine (Wurtz, Ann. Chim. Phys. [3] 55, 458; Hell and Wildermann, *l.c.*; Kondakoff, *l.c.*), and, when cautiously mixed with well-cooled sulphuric acid, sp.gr. 1·67 (2 vols. H_2SO_4 to 1 vol. water), in a freezing mixture, is converted into dimethylethyl carbinol, b.p. 101·6°–102°/762·2 mm., which has valuable hypnotic properties (J. Soc. Chem. Ind. 8, 1002; 9, 650, 889), and can be obtained, after neutralisation with sodium hydroxide; on distillation (Flavitzky, 175, 157) with sulphuric acid, sp.gr. 1·545 (2 pts. by weight H_2SO_4 to 1 pt. water), methyl*iso*propyl carbinol is obtained (Osipoff, Ber. 8, 542, 1240). Amylene forms compounds with metallic salts (Denigès, Compt. rend. 126, 1146; Kondakoff, J. Russ. Phys. Chem. Soc. 25, 35). When heated to high temperatures, benzene, naphthalene, acetylene, methane, carbon, and hydrogen are produced, the products depending on the temperature (Haber and Oechelhäuser (Chem. Zentr. 1897, i. 225). The action of nitrosyl chloride on amylene has been studied by Tilden and Sudborough (Chem. Soc. Trans. 1893, 482).

In addition to ordinary amylene, the following isomerides have been obtained:—*Normal amylene*, b.p. 39°–40° (Wurtz, Annalen, 123, 205; 127, 55; 148, 131; Zeidler, Annalen, 197, 253; Kondakoff, J. Russ. Phys. Chem. Soc. 24, 113; Flavitzky and Wyschnegradsky, *l.c.*); *isopropylethylene*, b.p. 21·1°–21·3° (Flavitzky and Wyschnegradsky, *l.c.*; Kondakoff, *l.c.*; Ipatieff, *l.c.*); *symmetrical methylethylethylene*, b.p. 36° at 740·8 mm. (Wagner and Saytzew, Annalen, 175, 373; 179, 302; Kondakoff, *l.c.*; Lissier, Bull. Soc. chim. 9, (3) 100); and *unsymmetrical methylethylethylene*, b.p. 31°–32°, sp.gr. 0·67 at 0° (Wyschnegradsky, *l.c.*; Le Bel, Bull. Soc. chim. 25, 546; Kondakoff, *l.c.* 25, 354); *Methyltetramethylene*, b.p. 39°–42° (Coleman and Perkin, Chem. Soc. Trans. 1888, 201); *pentamethylene*, b.p. 35° (Gustavson and Demganoff, J. Russ. Phys. Chem. Soc. 21, 344; Markownikoff, Ber. 30, 975; Young, Chem. Soc. Trans. 1898, 906; Wislicenus and Hanschel, Annalen, 275, 327); and *dimethyltrimethylene* (Gustavson and Popper, J. pr. Chem. 166, 458).

The action of hydrogen iodide on the amylenes has been investigated by Saytzew (Annalen, 179, 126); whilst Zeidler (Annalen, 186, 245) has examined the products obtained when various amylenes are oxidised with potassium permanganate in acid, neutral and alkaline solution, with chromic acid, and with potassium dichromate and sulphuric acid. The halogen derivatives of the various amylenes have been investigated (Lipp, Ber. 22, 2572; Hell and Wildermann, 23, 3210; Ipatieff, J. pr. Chem. 161, 257; Chem. Zentr. 1898, ii. 472; Brochet, Ann. Chim. Phys. 1897, 10, 381; Wassileef, Chem. Zentr. 1899, i. 775; Froebe and Hochstetter, Monatsh. 23, 1075; Kukuritschkin, J. Russ. Phys. Chem. Soc. 35, 873; Schmidt and Leipprand, Ber. 37, 532; Hamonet, Compt. rend. 138, 1609). Also the action of oxalic acid on various amylenes (Miklosheffsky, J. Russ. Phys. Chem. Soc. 22, 495), the nitrolamines (Wallach and Wohl, Annalen, 262, 324), and the nitrosites and nitrosates (Ipatieff, Chem. Zentr. 1899, ii. 178; Schmidt, Ber. 35, 2323, 2336, 3737; Hantzsch, 2978, 4120; Schmidt and Austin, Ber. 36, 1768).

The following polymerides of amylene have also been obtained, and can be prepared by heating ordinary amyl alcohol or amylene with zinc chloride:—*Diamylene* $C_{10}H_{20}$, b.p. 157°–157·5°/759 mm. (Balard, Annalen, 52, 316; Schneider, Annalen, 157, 207; Bauer, Jahresbericht. 1861, 660; Kondakoff, J. pr. Chem. 162, 442; Gasselin, Ann. Chim. Phys. 1894, 3, 5); *triamylene* $C_{15}H_{30}$ (Bauer, *l.c.*; Gasselin, *l.c.*); and *tetramylene* $C_{20}H_{40}$ (Bauer, *l.c.*). Also derivatives of diamylene (Schindelmeister, Chem. Zentr. 1896, ii. 354).

AMYLOCARBOL. · Trade name for a disinfectant, said to consist of carbolic acid 9 parts, amyl alcohol 160 parts, green soap 150 parts, water 690 parts.

AMYLOCOGULASE *v. Enzymes*, art. FERMENTATION.

AMYLOFORM. An antiseptic prepared by the action of formic aldehyde upon starch (Claassen, Pharm. Zeit. 41, 625) (*v.* SYNTHETIC DRUGS).

AMYRIN *v.* OLEO-RESINS.

ANACAHUITA. A wood of unknown botanical origin imported from Mexico; its preparations are said to be useful in pulmonary disorders. The wood contains a volatile oil, an iron-greening tannin, gallic acid, a yellowish resin, sugar, a tasteless volatile body crystallising in warty masses, and a bitter substance crystallising in white needles (J. 1861, 771).

ANACARDIUM NUT (Cashew Nut, Kajoo) is the fruit of *Anacardium occidentale* (Linn.), a tree indigenous to Brazil, Central America, and the West Indies. It has been transplanted to, and become naturalised in, many parts of India. The fruit rests on a fleshy edible peduncle, from which a spirit is distilled in Mozambique and in Western India. The nut is edible after it has been roasted to expel the cardol which it contains; the cardol thus obtained is used at Goa for tarring boats, and as a preservative of woodwork (Dymock, Pharm. J. [3] 7, 730). In addition to cardol, the nuts contain anacardic acid, and an oily matter which, by exposure to the air on linen, gives a brown stain, which is very permanent, but does not become black. It has been recommended as a marking ink, and is used for giving a black colour to candles (Böttger, Dingl. poly. J. 205, 490). From the stem of the plant a gum exudes which is said to be used by book-binders in South America.

The kernels contain 47·2 p.c. of a fatty oil, having the following characteristics:—Saponification value, 187; iodine value, 77–83·6; refraction in Zeiss' butyro-refractometer at 25°, 58·1–58·8 (Theopold, Pharm. Zeit. 1909, 1057).

J. L.

ANACARDIUM ORIENTALE (the 'marking nut tree') grows in the hotter parts of India, the West Indies, and in Northern Australia. It is now termed *Semecarpus anacardium*. As met with in commerce the nut is a black oval substance, from which, when cut, a black viscid juice exudes. This produces a light brown stain on linen, but gradually darkens on exposure to the air, and then resists the action of acids, alkalis, and chlorine. The native method of preparing marking ink, is to express the juice from the unripe fruit and to mix it with quicklime. The dried juice is also used in the preparation of a black varnish.

Kindt (Dingl. poly. J. 1859, 165, 158) prepared a marking ink from the nut by extracting it with a mixture of alcohol and ether, and evaporating the extract. This ink produced characters which, when moistened with a lime water or alkali solution, became black, and were then not completely removed when boiled with hydrochloric acid and potassium chlorate.

C. A. M.

ANÆSTHETICS. There are two principal types of anæsthesia, or loss of sensation sufficient to allow of surgical operations without pain. In *general* anæsthesia, total or partial insensibility and loss of muscular power are produced by the action of drugs on the brain, carried there in the circulation; extensive operations on any part of the body can then be done. In *regional* anæsthesia, insensibility to pain, with or without muscular paralysis, is produced by the action of anæsthetic drugs on the part where operation is contemplated. Regional anæsthesia can be produced (*a*) by the infiltration of the actual tissues to be lacerated with some substance which paralyses the endings of the nerves that convey painful sensations; (*b*) by a similar infiltration of the large or small nerve trunks supplying the field of operation; (*c*) by the injection into the spinal theca in the vertebral canal of a substance which paralyses the nerves, both sensory and motor, at their entrances into or exits from the spinal cord; (*a*) and (*b*) are usually classified together as *local* anæsthesia, while (*c*) is spoken of as *spinal* anæsthesia, which resembles general anæsthesia inasmuch as it causes loss of sensation and muscular power together over a wide region, and local anæsthesia in that consciousness is not lost and the anæsthetic is not diffused in the circulation.

Local anæsthetics. Very little is known of the action of these on the tissues with which they come in contact. They are all protoplasmic poisons which have a special preferential action upon nervous structures. Those in common use are: cocaine (methyl-benzoyl-ecgonine: $C_{17}H_{21}NO_4$); stovaine (hydrochloride of ethyl-dimethyl-amino-propinol benzoate); novocain (*p*-amido-benzoyl-diethyl-amino-ethenol-hydrochloride); tropacocaine (benzoyl-pseudo-tropeine-hydrochloride); β-eucaine (benzoyl-vinyl-diacetone-alkamine); β-eucaine lactate; alypin (hydrochloride of benzoyl-tetramethyl-diamino-ethyl-dimethyl-carbinol); quinine and urea hydrochloride; nirvanine (hydrochloride of diethyl-glycoll-*p*-amido-orthohydrobenzoic-methyl-ester); holocaine (hydrochloride of *p*-diethoxyethenyl-diphenyl-amidine); acoine (di-*p*-anisyl-mono-phenethyl-guanidine hydrochloride); orthoform (methyl-*p*-amino-meta-oxy-benzoate); anæsthone or anæsthesin (ethyl ester of *p*-aminobenzoic acid); apothesine (cinnamic ester of γ-diethyl-amino-alcohol hydrochloride).[1]

Braun has formulated postulates for appraising local anæsthetics. Omitting one which has not secured general assent, they are:

(1) Low toxicity in proportion to local anæsthetising power.

(2) Solubility in water to 2 p.c. at least; and stability of the solution, which should keep without deteriorating and be capable of sterilisation by boiling.

(3) Non-irritability to the tissues, and freedom from after-effects when absorbed into the circulation.

(4) Compatibility with suprarenal extract.

Acoine, holocaine hydrochloride, anæsthesine, and orthoform are more or less insoluble. Cocaine and eucaine are not soluble in water; but their salts, and the other drugs in the above list, are freely soluble and will keep without deteriorating. Cocaine solutions cannot be boiled, but stovaine, novocain, β-eucaine lactate, tropacocaine, alypin, and nirvanine can be thus sterilised, at 115° if necessary.

The most powerful anæsthetic action is that of stovaine. Next are cocaine, novocain, tropacocaine, alypin, and β-eucaine lactate, which are all about equal. The others have inferior actions in this respect. Experiments on mice and rabbits have resulted in the following table of relative toxicity, cocaine being taken as the unit[2]:—

Alypin, 1·25
Cocaine, 1·00
Nirvanine, 0·714
Stovaine, 0·625
Novocain, 0·490
β-eucaine lactate, 0·414

The irritant action of stovaine, tropacocaine, and β-eucaine lactate is greater than that of cocaine; that of novocain is less. All these five are compatible with suprarenal extract if the solutions are fresh mixed for each case. They are extensively employed; but novocain is evidently the best yet discovered for routine use.

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[1] Sir F. W. Hewitt and Dr. Henry Robinson's Anæsthetics and their Administration, 5th edit.

[2] Le Brocq, Pharm. J. 1909, 674.

Local anæsthetics are used dissolved in water or in normal saline solution. It is not essential that they should be injected subcutaneously; where the surface tissues are delicate, as on the eye, larynx, tongue, tonsils, simple contact with a local anæsthetic in solution or in fine powder will destroy sensation sufficiently for many surgical procedures. But elsewhere the solution is injected with a hypodermic syringe into the tissues which are to be rendered anæsthetic. If suprarenal extract be mixed with the anæsthetic solution, contraction of all the minute blood-vessels in the locality takes place. Thus the drug is retained longer in the tissues about the site of injection, instead of being rapidly dissipated in the lymph-stream. Consequently a more intense and lasting, because more strictly local, action occurs. The presence of 0·4 p.c. of potassium sulphate also intensifies the action of some local anæsthetics, especially of novocain.

Local anæsthesia can also be obtained by freezing the superficial tissues. A fine jet of ether or ethyl chloride is directed on to the desired portion of the skin, and when the latter is frozen a cut can be made, as for a whitlow, boil, or other small abscess, without causing pain.

Spinal anæsthetics. Some of the same drugs which cause local anæsthesia are available for injection into the cerebro-spinal fluid with which the spinal cord is surrounded in the vertebral canal. Stovaine is most used in Britain, but novocain and tropacocaine also are popular in Europe. The method was introduced by Bier in Germany in 1899, and since 1907 has been very extensively tried all over the world. The balance of opinion is that for ordinary cases spinal anæsthesia is too dangerous to replace general anæsthesia; but that for certain cases where the latter entails especial risks, it is of undoubted utility. Barker[1] and McGavin,[2] who are the most prominent advocates of spinal anæsthesia in England, use a solution of stovaine in 5 p.c. glucose. Of late years solutions which are as light as the cerebro-spinal fluid (sp gr. 1·006 to 1·007) have been extensively used, in place of the heavy glucose solutions. Many anæsthetists use morphine with or without scopolamine (hyoscine) as a preliminary, injected hypodermically.

General anæsthetics. There are many substances which diminish or abolish the perception of pain; but only a few of these are freely used as general anæsthetics. The conditions which must be fulfilled to obtain admission to the list are[3]:

(1) To produce absolute insensibility to pain without causing any great discomfort during induction.

(2) To produce loss of all voluntary and many reflex movements.

(3) To be capable of being readily introduced into the system, and rapidly eliminated, after the completion of the operation, without injury to the patient.

(4) To act in a regular and constant way, so that the effects can be controlled by the administrator.

The general anæsthetics in use in Great Britain are four in number: nitrous oxide, ethyl chloride, ether, chloroform. Ethyl bromide, ethidene dichloride (dichlorethane), bichloride of methylene, and amylene (pental) are obsolete. Hedonal (methyl-propyl-carbinol-urethane) and urethane itself have also been used as general anæsthetics, by direct injection in solution in normal saline into the blood stream.[1] In America and on the Continent anæsthol, somnoform, and narcotile are also employed. Anæsthol is a mixture of chloroform, ether, and ethyl chloride, in molecular proportions; somnoform is ethyl chloride 60 parts, methyl chloride 35 parts, ethyl bromide 5 parts; narcotile has been stated to be a compound, but analysis has shown it to be a mixture of methyl chloride, ethyl chloride, and ether. Mixtures of ether and chloroform in various proportions are in common use everywhere. Morphine, chloral, cannabis indica, and many other drugs have analgesic and anæsthetic properties; some of them, morphine especially, are used to assist the action of the volatile anæsthetics.

The effects of a general anæsthetic are produced by the circulation in the blood of the drug employed. When it reaches the brain the phenomena of anæsthesia are exhibited: at first slightly, then with increasing doses more and more intensely, until with a sufficient quantity death results. The phenomena of general anæsthesia are the same whether absorption takes place through the lungs, rectum, skin, blood stream, or gastro-intestinal tract. Thus alcohol has a marked anæsthetic effect, familiar in the indifference of a drunken man to injury.

The easiest way of introducing into the blood any substance which is a gas or a volatile liquid is by means of the lungs. The blood thus charged with an anæsthetic is rapidly delivered to the nervous centres, in which the essential changes of general anæsthesia take place. The absorption of vapours in the lungs varies with numerous factors: barometric pressure, temperature of the vapour and of the blood, rate of respiration, and rate of blood-flow through the pulmonary system. But the process is also something more than simple solution by diffusion of gases through a thin membrane; there is at least an element which depends on the fact that the tissues concerned are living.

The lungs are also the chief, but not the only, medium for the elimination of inhaled anæsthetics. These are but little decomposed during their tour of the circulation, and the greater part is discharged unchanged after the administration is suspended. What change they undergo in the blood is very uncertain. Chloroform, which has hitherto received more attention in this respect than the others, is recoverable from the blood in fatal cases of chloroform anæsthesia, but it is believed that most of it circulates in the red corpuscles of the blood in combination with the lecithin and cholesterin which they contain.[1] Glycuronic acid not uncommonly appears in the urine after chloroform anæsthesia. Nitrogen and sulphur are also excreted in the urine in greater quantity, indicating a greater destruction of proteid; and the increase of chlorides is held to show that some chloroform is decomposed in the body. The affinity of cholesterin and lecithin for chloroform, chloral, ether, sulphonal, tetronal, trional, and chloralamide has been suggested as the explanation for the selective action of these narcotics on the central nervous system, which contains a larger proportion of cholesterin and lecithin than do the other organs. With regard to ether, Turnbull states that etherisation produces a marked diminution of the hæmoglobin of the blood[2]; and Reicher finds three times the normal quantity of fat present in the blood, together with an increased amount of acetone, due to the disintegration of fat and albuminoid bodies.[3] The chemical composition of the blood is often much modified during anæsthesia, because the air supply to the lungs is frequently curtailed to a greater or less extent, and the elimination of CO_2 hindered. The proportions of O and CO_2 in the circulating blood may thus be altered at the expense of the former, and an asphyxial element added to the narcotic effect of the anæsthetic. Some authorities believe that deprivation of oxygen is the method by which all anæsthetics produce their action on the nervous tissues.

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[1] British Medical Journal, 1908, ii 453 (and other papers).

[2] Clinical Journal, March, 1914.

[3] R. W. Collum, The Practice of Anæsthetics, 1909. 14.

[1] Lancet March 23, 1912; and Brit. Med. Jour., June 15, 1912.

The chemical changes which may be assumed to take place in the brain during anæsthesia are unknown, as indeed are those of natural sleep. It has been suggested that unstable compounds are formed between the anæsthetic and the protoplasm of the nerve cells, and some observers describe changes recognisable microscopically in those cells as a result of anæsthesia. Professor Hans Meyer holds that there is a loose physico-chemical combination with the lipoids of the cell. This causes inhibition of the normal metabolism until the loose reversible combination breaks up. A rare sequel of chloroform anæsthesia is known as delayed chloroform poisoning. The symptoms of this condition, which is sometimes fatal, arise about eighteen to seventy-two hours after the anæsthesia. They are attributed to 'acidosis,' that is to diminished alkalinity of the blood due to the presence of acetone and aceto-acetic acid, which can be detected in the urine and the breath. For the developed condition sodium bicarbonate in large doses is employed; as a preventive measure feeding on glucose for a day or two before operation is found to answer best. Very rarely indeed this acidosis has followed the administration of ether.

Nitrous oxide (Laughing gas).—The inhalation of from three or four to twenty or thirty gallons of this gas without any air produces anæsthesia. If the administration is then suspended, insensibility lasts on an average about thirty to forty-five seconds, during which time minor operations such as the extraction of teeth can be undertaken. A marked asphyxial element is nearly always present, owing to the replacement of oxygen by N_2O. If air be admitted for brief periods between successive doses of gas, anæsthesia can be maintained without great difficulty for several minutes. By delivering nitrous oxide mixed with pure oxygen for inhalation, anæsthesia can be prolonged for any desired period. The proportions of the two gases are varied to meet the requirements of individual cases, but roughly the mixture must contain about 80 p.c. by volume of N_2O. This method is well suited for operations on the limbs, but for abdominal operations it is difficult to get the complete muscular relaxation necessary. Nitrous oxide gas is the safest known general anæsthetic, and recovery takes place very rapidly (two or three minutes) without unpleasant after-effects. Nitrous oxide for anæsthetic purposes should be entirely free from other oxides of nitrogen, and from chlorine; small quantities of H_2O, O, and N are usually present as impurities, and are of no moment.

Ethyl chloride.—The vapour of 3 to 5 c.c. of this substance allowed to volatilise in a closed chamber, such as a rubber bag, into which an adult patient exspires and from which he inspires, produces anæsthesia very rapidly. If administration is then suspended, insensibility lasts from one to two minutes. By administering a further dose before recovery takes place from the first one, anæsthesia can be prolonged; it is preferable, however, to give ether or chloroform or nitrous oxide and oxygen if a longer anæsthesia is required. The after-effects of ethyl chloride are intermediate between those of nitrous oxide and those of ether and chloroform. Ethyl chloride given by an expert is safer than either of the latter, but not so safe as nitrous oxide. No impurities can be tolerated in ethyl chloride for use as a general anæsthetic; there is no difficulty in securing complete purity.

Ether.—About 30 p.c. of air and 70 p.c. of ethereal vapour will produce and maintain general anæsthesia. The vapour is so intensely irritating to the mucous membrane which lines the mouth, nose, and air-passages, that it must first be offered very dilute, and then in a gradually increasing percentage. Limitation of air supply renders it possible to procure anæsthesia with a much smaller quantity of ether than when fresh air is freely admitted, for a slight concurrent asphyxia helps the action of the ether. Such asphyxiation has disadvantages of its own if allowed to exceed a very moderate degree; it is usually present during anæsthesia under ether by the 'closed' methods. There is slightly more difficulty in producing anæsthesia by the 'open' method, in which air enters freely; the preliminary injection of small doses of morphine ($\frac{1}{6}$ to $\frac{1}{4}$ grain) with atropine ($\frac{1}{200}$ to $\frac{1}{100}$ grain) is often practised. Ether is much less dangerous to life than chloroform in the operating room; but part of this advantage is counterbalanced by the occasional development of bronchitis and broncho-pneumonia afterwards. Ether for anæsthetic purposes should have a sp.gr. between 0·720 and 0·722. Provided impurities have been removed, it is of no significance whether rectified spirit or methylated spirit is used in the manufacture.

Chloroform.—Much research has been carried out to determine the percentage of chloroform necessary to produce anæsthesia by inhalation.

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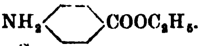
[1] Hale White, Materia Medica, 11th ed. 1909, 280.
[2] Laurence Turnbull, Artificial Anæsthesia, 228.
[3] Reicher, Lancet, Jan 25, 1908, 268.

Vernon Harcourt introduced early this century a chloroform inhaler capable of regulating this proportion up to 2 p.c. Experience showed that in occasional cases it is very difficult or impossible to induce anæsthesia with this amount, and a modification of the instrument allows air to be inspired containing 3 p.c. In practically every case anæsthesia, when fully established, can be maintained with a 2 p.c. vapour. Alcock, who has investigated the dosage of chloroform very carefully, finds[1] that for an ordinary adult it suffices to offer a percentage rising gradually to 2½ in three minutes; this as a rule produces complete surgical anæsthesia in eight or ten minutes. If a higher proportion is necessary, 3 p.c. may be allowed at the end of five minutes. He finds that within a few minutes after induction is complete 1·5 p.c., and after half an hour 1 p.c., will usually be enough. Several physiologists have estimated the amount of chloroform in the circulating blood during anæsthesia: their results vary from 0·035 to 0·07 p.c. Chloroform is the least safe of these four anæsthetics, especially in the hands of those whose experience as anæsthetists is small. Chloroform for anæsthetic purposes is found to keep better if it contains 0·2 to 0·5 p.c. of alcohol or of ethyl chloride. No other impurities are tolerable. It is also less liable to decomposition if kept in the dark. There are three commercial processes of manufacture, based respectively upon rectified spirit, methylated spirit, and acetone; there is no difference between the actions of the resulting chloroforms, provided they are duly purified. H. R.

ANÆSTHESINE. Trade name for ethyl *p*-amino-benzoate 

ANAGYRINE *v.* CYTISINE.

ANALUTOS or **KALMOPYRIN.** Trade names for calcium acetyl salicylate.

ANALGESINE. Identical with antipyrine (*q.v.*).

ANALYSIS. Chemical analysis is the separation of a complex material into simpler constituents. It is *ultimate* when these component parts are elementary forms of matter, and *proximate* when the subdivision consists only in the separation of the original substance into less complicated compounds. The aim of chemical analysis is twofold: the first object is to ascertain the nature of the components of a mixture or complex substance; the second is to determine the proportions in which these constituents are present. All analytical operations may therefore be classified under the two main categories of *qualitative* and *quantitative* analysis, according as to whether these processes lead to the identification of the proximate or ultimate constituents of a complex substance, or to the determination of the relative proportions in which these constituents are present.

This article is written primarily from the technical point of view, and accordingly the descriptions given in the qualitative section are restricted mainly to those elements which find application in the arts and industries. Similarly, the estimations and separations outlined in the quantitative section are chiefly those required in the analysis of technically important materials.

The systematic investigation of the individual elements and their typical compounds has revealed the existence of many characteristic reactions which are exhibited by certain elements and compounds under widely varying conditions of combination or association. This circumstance leads to a simplification which is utilised extensively in both qualitative and quantitative analysis. In qualitative work, such characteristic reactions as are not generally interfered with by other substances enable the analyst to detect the presence of certain elementary or compound substances without undertaking the more laborious processes involved in isolating these constituents from the other ingredients of a mixture.

In quantitative analysis two essentially different methods of procedure are employed, the more fundamental one being *gravimetric* analysis, in which the elementary or complex constituent of a mixture is isolated and weighed in the form of a definite compound. By utilising quantitatively the above-mentioned distinctive reactions it is frequently possible to adopt the second procedure known as *volumetric* analysis, in which the relative amount of a certain constituent is estimated in the presence of other elements and compounds associated with this constituent in the mixture under examination.

For the purposes of scientific investigation the most accurate methods are essential, and these are, in the main, gravimetric in character; but for technical requirements extreme accuracy is rarely required, and rapid methods giving approximately correct results are preferred to more exact processes involving a longer time for their execution. It is in this direction that volumetric analysis has been most extensively developed, the general tendency in industrial laboratories being to replace gravimetric methods by quicker volumetric processes with very little loss in accuracy, provided that certain essential conditions be fulfilled.

General Operations.

Sampling.—It is of the highest importance that the sample under examination should be truly representative of the bulk of the substance. Discrepancies between the results of different analysts are usually attributed to faulty methods or inaccurate work, but in many cases they are really due to imperfect sampling. If the substance is a liquid, the contents of the vessel should be thoroughly mixed before the sample is withdrawn. If the substance is contained in several vessels, a proportional quantity should be taken from each, the different portions mixed together, and the final sample taken from the mixture.

In the case of solid products care must be taken to secure a proper proportion of large and small, hard and soft fragments. If a ship's cargo is to be sampled, portions should be taken from different parts of the bulk; if the substance is contained in railway trucks, portions should be taken from the ends and middle of each truck. When the substance is in bags or barrels, a long hollow auger is thrust to the bottom of each and then withdrawn, bringing with it a long core of the substance. If the material loses or gains moisture, or undergoes any other change on exposure to air, as in the case of soap or caustic soda, a proper proportion of the internal and external portions must be taken. In all cases the first samples are broken into small pieces, thoroughly mixed, and one-fourth taken for further treatment. This is ground to powder, again thoroughly mixed, and one-fourth taken. The subdivision is repeated, if necessary, and the final sample kept in well-closed bottles. This process of 'quartering' may also be effected by spreading out the finely powdered material in the form of a flattened cylinder dividing this radially into four parts, taking out the opposite sectors, mixing these thoroughly, and repeating the subdivision.

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[1] N. H. Alcock. British Medical Journal, Feb. 6, 1909, 325.

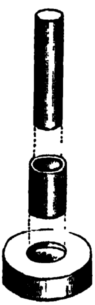


Fig. 1.

If the mixture is soft and friable, pulverisation is readily effected in a porcelain or earthenware mortar, but harder substances should be powdered in a cast-iron or steel mortar. When the substance is hard, and a very fine powder is required, an agate mortar should be used for the final operation, so that the powder may be completely sifted through fine muslin. Very hard substances, such as minerals, are first broken into small pieces by wrapping them in paper and striking with a hammer, and are then further crushed in a steel mortar (Fig. 1) consisting of a strong base with a circular recess into which fits a movable steel ring or guard, and inside this is a solid steel piston which acts as a pestle. A small quantity of the mineral is placed on the base of the mortar inside the guard-ring, the latter is held firmly down, and the piston is placed inside and struck smartly with a hammer, which drives it down upon the mineral. The final crushing is done in an agate mortar.

The mechanical ore-grinder described in Hillebrand's Analysis of Silicate and Carbonate Rocks, may likewise be employed in reducing hard minerals to a fine powder.

Drying.—Many substances absorb more or less moisture when exposed to the air, and in order to bring them into a definite condition for analysis, it is desirable that they should be dried, this operation being conducted at the ordinary or at a higher temperature according to circumstances. Substances which contain water in combination are usually dried by exposure to air or by pressure between folds of filter paper. In other cases where a higher temperature would be injurious the substance may be placed under a bell-jar which also incloses a dish containing sulphuric acid. The operation proceeds more quickly if the bell-jar is connected with an air-pump and thus rendered vacuous.

Substances which do not decompose at 100° are best dried in a copper oven provided with a jacket containing water which is heated to boiling, the water-level being kept constant by means of an overflow *a* and feeding arrangement at the side. The inside of the oven is fitted with a perforated shelf which supports dishes, funnels, &c. (Fig. 2).

When the substance is sufficiently stable it is advisable to dry at 115°–120°, since an increase of 10° or 20° often greatly reduces the time required For this purpose we use a copper oven without a jacket, heated by a lamp underneath; or toluene, boiling at 110°, may be used instead of water in the oven with a jacket, crude xylene will give a higher temperature (120°). Inside the oven at a little distance from the bottom is a shelf which supports the vessel containing the substance. At the top of the oven are two apertures, one of which serves to promote a current of air through the oven, whilst the other carries a thermometer the bulb of which is close beside the vessel which is being heated (*cf.* Huntly and Coste, J. Soc. Chem. Ind. 1913, 32, 62).

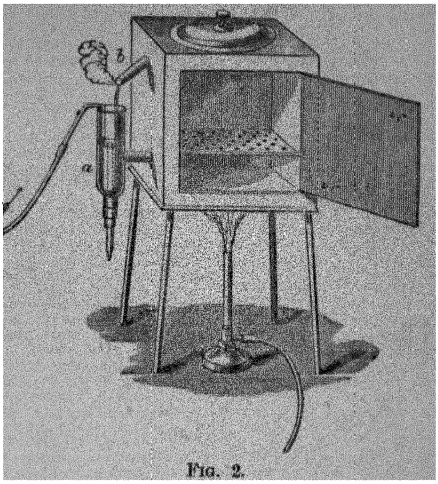


Fig. 2.

If it is desired to keep the temperature constant for a long time, the oven must be provided with a thermoregulator (*v.* THERMOREGULATORS).

Weighing.—The balance and the precautions to be observed in weighing form the subject of a special article (*v.* BALANCE). As a rule, substances taken for analysis should be weighed from tubes provided with well-fitting stoppers or corks, or from weighing bottles fitted with glass capsule stoppers, the difference between the weight of the tube or bottle before and after the removal of the substance giving the weight taken for analysis. The quantity required for an analysis will depend upon circumstances. When constituents present in minute quantity have to be estimated, a relatively large amount of the substance is required, but for the estimation of one or two constituents from 1 to 2 grams of the substance is usually sufficient. The smaller the quantity of matter operated upon, the shorter the time required for filtration, washing, &c., but also the greater the demands on the skill and accuracy of the operator.

Hygroscopic substances and precipitates must be kept under a *desiccator* (*q.v.*), *i.e.* a glass dish containing sulphuric acid or calcium chloride, fitted with a tray to support a crucible, &c., and provided with an air-tight glass cover, preferably bell-shaped. Crucibles containing non-hygroscopic precipitates may be allowed to cool with exposure to air, provided that the empty crucibles were allowed to cool under the same conditions before weighing.

Solution.—The solution of a substance is most conveniently effected in flasks or in somewhat deep beakers which are inclined at an angle in order to prevent possible loss by spurting. The operation may be accelerated by heat, and the reagent should be used in the most concentrated form possible and in the least possible excess, in order to avoid loss of time in evaporation, &c. Evaporation to expel excess of solvent should, where possible, be conducted in the same vessel.

Evaporation.—The evaporation of a liquid may be effected over an ordinary bunsen flame, or over a rose burner, care being taken that the liquid does not boil. If the operation is conducted in a flask or crucible, the latter should be inclined in order to prevent loss by ebullition, and the operation is accelerated in the first case by drawing a current of air through the flask, in the second by inclining the lid of the crucible (Fig. 3) across the mouth of the vessel and thus producing a circulation. The rate of evaporation, *cæteris paribus*, depends on the area of surface exposed, and hence the operation is effected most quickly in shallow dishes, especially if a current of air removes the vapour as fast as it is given off. During the process the contents of the dish should be protected from dust, &c., and this is really done by supporting at a distance of about six inches above the surface of the dish a triangle of glass rod or tubing on which is stretched a sheet of filter paper freed from soluble compounds by treatment with acid. When evaporation over a direct flame is impracticable, the dishes, &c., should be placed on a *water-bath*, that is, a vessel containing boiling water, in such a way that they are heated by the steam. The top of the water drying-oven already described (Fig. 2) may be provided with a series of rings of various sizes and thus serves two purposes. Ordinary tin cans or copper vessels of similar shape will answer, but in all cases it is desirable to have an arrangement for keeping the water at a constant level.

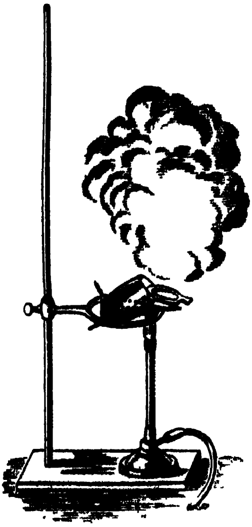


FIG. 3

Precipitation is conducted in beakers, dishes, or conical flasks, but not in ordinary round flasks because of the difficulty of removing the precipitate. Glass vessels, especially when new, are appreciably attacked and dissolved by water, and still more strongly by alkaline solutions, the action increasing with the concentration of the solution and the duration of contact. For quantitative work Jena glass vessels should be used, as these are least affected by alkalis. Acid liquids, with the exception of dilute sulphuric acid, have less solvent action. Porcelain vessels, especially after they have been used for a short time, are not appreciably attacked (Fresenius's Quant. Anal.). All precipitations involving long heating with alkaline liquids should be conducted in porcelain vessels or in platinum, silver, or nickel dishes. Silica-ware vessels can be used with all acid liquids excepting those evolving hydrogen fluoride (Zeitsch. anorg. Chem. 1905, 44, 221).

Unless circumstances forbid, the liquid and the reagent should be heated to boiling and mixed gradually with continual agitation, since under these conditions precipitation as a rule is more rapid and complete, and the precipitate is obtained in a dense and granular form and is readily separated and washed. Usually filtration may be commenced as soon as the supernatant liquid is clear, or at any rate after two or three hours. An unnecessary excess of reagent should always be avoided, but in all cases complete precipitation should be proved by adding a small quantity of the reagent to the clear liquid.

Filtration.—The separation of a precipitate from a liquid is usually effected by means of a specially prepared variety of blotting paper, known as filter paper. The Swedish paper made by J. Munktell has the oldest reputation, but that known as Whatman paper, made by W. & R. Balston, Ltd., is of excellent quality, and for many purposes answers better. The latter firm supply paper which has been treated with hydrochloric and hydrofluoric acids, and thus freed from almost all inorganic matter. It is desirable that all paper used in quantitative work should be free from soluble compounds, and this end is secured by soaking the ordinary filter paper for three or four hours in pure hydrochloric acid diluted with 15–20 times its volume of water, and then washing thoroughly to remove all traces of acid and soluble salts. The paper is conveniently kept in circular pieces of known radii (2, 4, 5, 6, 8 cm.), and the ash left by each size should be determined once for all by incinerating six filters of one of the medium sizes in the manner described under the treatment of precipitates, and weighing the ash which is left. This quantity divided by six gives the average amount of ash left by one filter of that size, and the amount left by the other sizes is readily calculated, the quantity of ash being proportional to the area of the paper.

Usually the filter paper is supported in a glass funnel which should have smooth even sides and an angle of 60°. The stem should be somewhat long and not too wide, with the lower end cut obliquely. A circular filter is folded in half, then in a quadrant, and when the quadrant is opened at one side it forms a hollow cone which should fit accurately into the funnel. The edge of the filter paper should be about 10 mm. below the edge of the funnel, and the size of the filter should be such that it is not more than three quarters filled by the precipitate. After placing the filter in position it is moistened with water, and fitted accurately to the glass, care being taken to remove all air bubbles from between the glass and the paper. Attention to these points greatly facilitates the subsequent filtration. The edge of the vessel containing the liquid to be filtered is slightly greased outside, and the liquid is directed into the filter by means of a glass rod, care being taken not to disturb the precipitate until most of the clear liquid has passed through. It is advisable to keep the filter well filled with the liquid, but the latter must not rise higher than 10 mm. below the top of the paper.

In order to accelerate filtration a glass tube about 3–4 mm. in diameter and not less than 20 cm. long, bent into a loop near its upper end, may be attached to the stem of the funnel by means of indiarubber tube.

Greater rapidity of filtration is obtained by using one of the numerous water pumps (*v.* Filter pump). In this case the liquid is filtered into a flask with stout walls, preferably of the conical form. The stem of the funnel passes through a cork which fits in the neck of the flask and also carries a tube connected with the pump, or the flask may be provided with a side tube for this latter purpose. When it is required to filter into a dish or beaker, the latter is placed under a tubulated bell-jar standing on a glass plate, the cork carrying the funnel, &c., being fitted into the tubulus of the bell-jar. If the reduction of pressure is considerable, it becomes necessary to support the apex of the filter. In the case of filters of medium size the necessary toughness is obtained by dropping into the apex of the dry filter, after it has been fitted into the funnel, two or three drops of the strongest nitric acid. After a minute or two the paper is washed and is ready for use. Bunsen's original method is to support the apex of the filter by means of a cone of platinum foil, which is made in the following way. A circular piece of thin platinum foil 3–4 cm. in diameter is cut in the manner shown in the diagram (Fig. 4), softened by heating in a flame, and then placed against a small metal cone of 60°, so that the point *a* coincides with the apex of the cone. The foil is then folded round the metal so that it also forms a small cone, which is finished by being pressed in a hollow conical mould into which the metal cone fits. It is then dropped into the funnel and the paper fitted in. The metal cones and moulds required can be purchased; Bunsen's method of making a cone and mould of plaster is described in Thorpe's Quantitative Analysis.

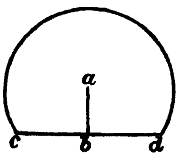


Fig. 4.

Carmichael has described a method of reverse filtration (Zeitsch. anal. Chem. 10, 83).

The Gooch crucible (Chem. News, 37, 181), which has a perforated bottom lined with a thin asbestos mat, has now become a recognised means of collecting precipitates. The asbestos makes an excellent filter, is not affected by ordinary acid and alkaline liquids, is readily dried, and does not alter in weight when ignited. The quality of the asbestos is of prime importance, a non-ferruginous amphibole being preferable to the cheaper hydrated varieties of serpentine which are appreciably soluble in acids. Silky asbestos is scraped into a short fine down, boiled with hydrochloric acid, well washed, and kept in water. A platinum or silica crucible, preferably of the low wide form, with the bottom perforated with a large number of minute holes, is fitted air-tight into an ordinary funnel by means of an indiarubber ring placed between the crucible and the wall of the funnel, which is fitted into a filtering flask. The pump is set in action and water containing the asbestos in suspension is poured into the crucible. A layer of asbestos felt is quickly formed, and when this is of sufficient thickness it is drained, dried, and ignited over a lamp, and the crucible is then weighed. It is desirable to have a non-perforated bottom to fit on the crucible during ignition, in order to protect the contents of the crucible from the flame gases. A Soxhlet tube, having a perforated porcelain or platinum disc covered with an asbestos layer and supported at the constricted part of the tube, is frequently used to collect precipitates. Neubauer recommends a perforated platinum crucible with a felted platinum mat (Zeitsch. anorg. Chem. 1901, 922; *cf.* Amer. Chem. J. 1909, 31, 456). The weighed crucible is replaced in the funnel, and filtration is conducted in the ordinary way, care being taken that the pump is set in action before any liquid is poured into the crucible. Drying and igniting the precipitate occupies but little time. For gelatinous precipitates the crucible may be replaced by a cone, the lower part of which is made of platinum gauze and the upper part of platinum foil.

Gooch has proposed (P. Am. A. 1885, 390; Zeitsch. anal. Chem. 24, 583) in special cases to replace the asbestos by anthracene, which after filtration can be dissolved in benzene or other suitable solvent, leaving the precipitate undissolved.

Not unfrequently it is necessary to keep the contents of a funnel hot during filtration. This is effected by placing the funnel inside a copper jacket filled with water which is heated to boiling by means of a side tube. A simpler plan is to coil lead pipe round the funnel and blow steam through the pipe (Richter, J. pr. Chem. (ii.) 28, 309).

Sometimes it is desirable to avoid contact with air during filtration. A convenient apparatus for this purpose has been described by Klobukow (Zeitsch. anal. Chem. 24, 395; J. Soc. Chem. Ind. 4, 756).

All precipitates require to be washed in order to remove soluble impurities, the liquid employed being water, dilute acid, dilute ammonia, alcohol, &c., as the case may require. The object in all cases is to reduce the impurity to the desired minimum in the shortest possible time with the least expenditure of liquid, and it can readily be shown that successive treatments with small quantities of the liquid are far more effectual than the same volume of liquid applied all at once (Bunsen, Annalen, 148, 269). When ever possible hot liquids should be used, and the precipitate should be washed so far as possible by decantation, only the washing liquid being poured on the filter. The soluble impurity collects round the top edge of the filter paper by reason of capillary action and evaporation, and hence, when washing is effected with the aid of an ordinary wash-bottle with a movable jet, it is important that the liquid should be directed on to the top edge of the filter. It is also important that each quantity of wash-water should be drained away as completely as possible before adding a fresh quantity, and it is obvious that this takes place most readily when a pump is used. In this case the liquid is poured into the funnel from an open vessel to a height of about 10 mm. above the edges of the paper. Care must be taken that the precipitate is not drained so far that channels are formed. It is always advisable to ascertain whether the washing is complete by testing a few drops of the last wash-water.

Drying and weighing precipitates.—Occasionally a precipitate must be dried without the application of heat, and this is accomplished in a desiccator over sulphuric acid, preferably in a vacuum. In other instances the substance is not injured by a temperature of say 120°, but cannot be ignited. In these cases the filter is carefully dried at the particular temperature, enclosed between a pair of watch-glasses, and weighed. It is then placed in the funnel and the operation proceeded with. After filtration the filter and the precipitate are thoroughly dried at the same temperature as before and again weighed, the increase being the weight of the precipitate. Tared filters can, however, be generally replaced by Gooch crucibles, Soxhlet tubes, &c. The majority of the precipitates usually met with can, moreover, be dried by heating them in a crucible over a lamp. In most cases it is not necessary that the precipitates should previously be dried. The greater part of the water is removed by draining in the funnel by means of the pump or by placing the filter and its contents on a porous tile or on a pad of filter paper. The filter is then introduced into a crucible, heated cautiously until quite dry and then heated more strongly until the weight is constant.

When the precipitate is not easily reducible it is not necessary to remove the paper before ignition. The wet paper enclosing the precipitate is placed in a platinum crucible, and the latter heated with a full flame; the water present assumes the spheroidal state and the paper smoulders away without spurting. If any slight reduction takes place, for example, with barium sulphate, it is easily remedied by adding a few drops of dilute sulphuric acid and again heating. In the case of magnesium pyrophosphate strong nitric acid serves a similar purpose. If, however, the precipitate is readily reduced in contact with organic matter, it must be removed from the paper as completely as possible by gentle friction, and transferred to the crucible, which should stand on a sheet of glazed paper. A carefully trimmed feather or a camel's-hair brush is useful to transfer scattered particles from the paper to the crucible. The filter paper is then folded with the portion to which the precipitate had adhered inside, wrapped in platinum wire which forms a sort of cage, and set on fire. Whilst burning it is held over the crucible, and *when completely burnt out*, the ash is heated with the tip of a Bunsen flame for a few minutes and then shaken into the crucible.

Precipitates which contain compounds of silver, lead, zinc, tin, and other easily reducible metals, should be heated in porcelain crucibles, since platinum vessels are liable to be attacked. Care should also be taken that platinum vessels are not heated with smoky or 'roaring' flames, and do not come in contact with brass crucible tongs or easily fusible metals whilst hot. After some time the surface of the metal may become dull, owing to the partial disaggregation of the platinum, but this defect can be remedied by polishing the metal with sea-sand or a burnisher.

Heating appliances.—The ordinary bunsen burner serves for most operations, but the argand bunsens introduced by Fletcher are more efficient, and the radial slit burner of the same inventor is perhaps the most efficient gas-burner for heating purposes that has yet been made. Glass vessels are more safely heated on a sheet of wire gauze or on a layer of sand in a metal tray. A most useful piece of apparatus in a technical laboratory is a large iron plate supported on iron legs, and heated by a burner underneath the middle. Vessels placed on the plate near its edges are subjected to a very gentle heat, but may be raised to a much higher temperature by being moved nearer to the middle.

A water-bath provided with a constant feeding arrangement is the most useful way of heating vessels at 100°. If higher temperatures are needed, a saturated solution of calcium chloride, melted paraffin, or oil may be used. Maumené (Compt. rend. 1883, 97, 45, and 215) has proposed to use fused mixtures of alkaline nitrates for temperatures between 140° and 250°. Brauner (Chem. Soc. Trans. 1885, 47, 887) has described a simple arrangement for heating substances in sulphur vapour.

Reagents.—The ordinary acids and ammonia are required in a dilute as well as in a concentrated form. Whenever possible the reagents should be made in solutions the strengths of which are multiples or submultiples of normal solutions. A convenient strength for the dilute mineral acids is twice normal, and the alkaline solutions should be of equivalent strength.

QUALITATIVE ANALYSIS.

The detection of the constituents of a mixture or chemical substance is based on the fact that almost every metallic or acidic radical will under suitable conditions give rise to a reaction which, under these conditions, is characteristic and thus enables one to distinguish this radical from all others. These tests may be applied directly to the solid substance, usually at high temperatures, when they are known as *dry reactions*; or they may be employed in solution, in which case they are described as *wet reactions*. The wet and dry reactions of metallic and acidic radicals are generally, but by no means invariably, independent of the acidic and

metallic radicals with which they are respectively combined.

Examination in the Dry Way.

The indications obtained from the dry reactions of a substance frequently afford very suggestive clues to its composition, but as these tests rarely, if ever, indicate the relative proportions in which the constituents exist in the mixture under examination, they must be regarded as being preliminary to the more systematic examination of the substance in solution. Moreover, negative results obtained from dry tests must not be accepted as final evidence.

In all cases, however, a preliminary examination of the substance should be made in the dry way, and if the substance is in solution a portion should be evaporated to dryness. The reactions of several substances in the dry way are interfered with and rendered inconclusive by the presence of certain other substances; but nevertheless an examination of this kind often gives much information in a short time.

The most convenient source of heat for this purpose is the ordinary bunsen burner. This consists of a metal tube at the base of which coal gas enters by means of a jet, the lower part of the tube being pierced with holes through which air is drawn and mixed with the coal gas. The mixture of 1 volume of coal gas with about 2½ volumes of air, which is thus produced, burns at the top of the tube with a non-luminous flame. When the supply of gas is turned low, it is necessary also to reduce the air supply by partially closing the inlet holes by means of a regulator. The upper part of the burner is generally fitted with a support carrying a cone to protect the flame from draughts.

The flame consists essentially of an inner dark zone containing unburnt gas mixed with air, and an outer zone or flame mantle in which combustion becomes complete. If the air holes are partially closed, a luminous cone appears at the top of the inner zone. Bunsen has shown, however, that several distinct zones exist, each of which can be utilised for producing particular reactions. The most useful of these are *a*, a comparatively cold zone at the base of the flame, which serves for the volatilisation of salts in order to obtain flame colourations; the *lower reducing flame* δ about one quarter of the way up and close to the edge of the dark zone; η, the *upper* and more powerful *reducing flame* at the top of the dark zone, obtained by closing the air holes until the tip of the inner zone just becomes luminous; β, the *zone of fusion* or highest temperature, at about one-third the height of the flame and half-way between the inner zone and the flame mantle; γ, the *lower* and hotter *oxidising flame* at the edge just below the zone of fusion; and ε, the *upper oxidising flame* at the extreme tip of the flame.

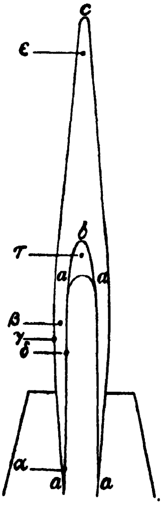


FIG. 5.

Instead of the bunsen burner, the flame obtained by means of a blowpipe may be used; a mouth blowpipe consists of a metal tube provided at one end with a mouthpiece, the other end fitting into a small metal box which serves to condense and retain the moisture of the breath. From the side of this box a second shorter and narrower tube projects at right angles to the first, and is provided with a nozzle or jet of brass or, better, of platinum. For general work the diameter of the bore of the jet should be 0·4 mm. In Black's blowpipe the larger tube is conical, the lower and wider end serving the same purpose as the box in the form just described. The art of keeping up a continuous blast of air through the blowpipe can only be acquired by practice. The necessary pressure is produced by distending the cheeks, breathing being carried on through the nostrils, whilst communication between the nostrils and the mouth is cut off by the pressure of the tongue against the palate. A convenient form of hand-blower for blowpipe work has been devised by Fletcher.

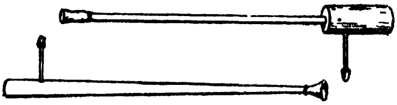


FIG. 6.

A good flame for blowpipe work is obtained by dropping into the tube of an ordinary bunsen burner a brass tube, the lower end of which descends to the bottom of the burner and cuts off the supply of air, whilst the upper end is flattened and cut off obliquely. The flame should be much smaller than when the burner is used in the ordinary way. Coal gas usually contains more or less sulphur, and consequently cannot be used when testing for this element.

A thick stearin candle answers well; but nothing is better than a lamp consisting of a low and rather wide cylindrical metal vessel, open at the top, with a somewhat broad and flat wick-holder attached to the side. The fuel used is solid paraffin, which is kept in a melted condition by the heat of the blowpipe flame, the wick being so arranged that the flame passes over the top of the paraffin. A metal cover protects the lamp from dust when not in use.

The nozzle of the blowpipe is introduced a short distance into the lamp flame at a short distance above the wick, and when the blast is produced the flame is deflected horizontally, becomes long and narrow, and is seen to consist of two parts, viz. an *outer* or *oxidising* flame, at the tip of which there is an excess of oxygen heated to a high temperature, and an *inner* or *reducing* flame, which contains carbonic oxide and hydrocarbons heated to a high temperature. If the blowpipe is held just at the edge of the flame and a moderate blast is used, a broader

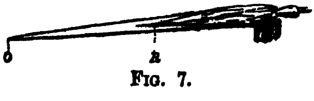


FIG. 7.

reducing flame can be obtained, which has a luminous tip containing solid particles of carbon.

The following appliances are required: a small pair of forceps with platinum points; short pieces of thin platinum wire; charcoal from some fine-grained compact wood; glass tubes about 3 mm. internal diameter, and 60–80 mm. long, closed at one end; and glass tubes of similar diameter 100–120 mm. long, open at both ends and bent slightly in the middle. The reagents used are borax, microcosmic salt ($NH_4NaHPO_4, 4H_2O$), potassium cyanide, sodium carbonate, potassium nitrate, cobalt nitrate solution, and potassium hydrogen sulphate.

The dry tests are conveniently performed in the following order:—

(1) *Heating in a dry closed tube.*—To avoid soiling the sides of the tube, the substance should be introduced by means of a roll of stiff paper. The following changes may be observed:

(*a*) Carbonisation with or without evolution of empyreumatic vapours = *organic compounds.*

(*b*) Condensation of moisture on cold parts of tube; neutral reaction = *hydrated salts and hydroxides*; acid reaction = *acids and acid salts*; alkaline reaction = *ammonium salts.*

(*c*) Fusion without change of colour = *alkaline salts, hydrated salts.*

(*d*) Fusion with change of colour = yellow hot, dark yellow cold = *bismuth oxide*; yellow hot, red cold = *lead oxide*. The chromates of lead and the alkali metals fuse and darken on heating.

(*e*) No fusion, but change of colour: dark yellow hot, pale yellow cold = *stannic oxide*; yellow hot, white cold = *zinc oxide*; black hot, reddish-brown cold = *ferric oxide*; black hot, bright red cold = *mercuric oxide*; brown darkening on heating = *cadmium oxide.*

(*f*) Gas evolved: oxygen = *oxides, peroxides, chlorates, bromates, perchlorates, iodates, periodates, persulphates,* and *nitrates*; carbon dioxide = *carbonates, bicarbonates, oxalates*; carbon monoxide (blue flame) = *formates, oxalates*; sulphur dioxide = *acid sulphites, sulphates of heavy metals* (together with sulphur trioxide); cyanogen = *cyanides of heavy metals*; ammonia = *ammonium salts*; phosphine = *phosphites, hypophosphites*; orange-brown vapours = *nitrates, nitrites, bromides*; violet vapours = *iodides*; colourless fuming gas = *hydrated chlorides.*

(*g*) Sublimate: white infusible = *arsenious oxide* (octahedra), *antimonious oxide* (needles), *selenium dioxide, ammonium chloride, ammonium sulphite* (from ammonium sulphate); white fusible = *mercuric chloride, tellurium dioxide, organic acids, molybdenum trioxide* (at very high temperatures); coloured, black, or reddish black = *selenium, mercuric sulphide*; yellow hot, red cold = *mercuric iodide*; reddish yellow = *arsenious sulphide*; yellow = *sulphur* and *sulphides*; black metallic mirror = *arsenic*; grey metallic globules = *mercury.* These metallic sublimates are often obtained more readily by heating the material with potassium cyanide.

Phosphorus compounds are detected by heating in a closed tube with magnesium ribbon and dropping the hot tube into water, when inflammable phosphine is evolved.

(2) *Heating in open tube.*—The tube being inclined, to promote a current of air through it, the changes observed are similar to the reactions in the closed tube, but sulphides burn evolving sulphur dioxide; arsenic is oxidised to arsenious oxide, and selenium and its compounds evolve a pungent odour of horseradish (dioxide), and give a grey or reddish sublimate.

(3) *Heating on platinum wire.—Flame colourations.*—The wire being cleaned by repeated dipping in hydrochloric acid and heating till it imparts no colour to the flame, a small quantity of the substance supported on the end of the wire is introduced into zone *a* of the bunsen flame. As a colouration is produced only if volatile compounds of the metals are present, the substance should be moistened with hydrochloric acid to produce the volatile chlorides. This result may also be attained by mixing the substance on an asbestos thread with moist silver chloride, a compound which, while imparting no colour to the flame, slowly yields chlorine, converting other metals into chlorides. The wire should be slowly moved into the hottest part of the blowpipe or bunsen flame, so that the colourations due to less volatile constituents may be successively developed.

Colourations: yellow = *sodium*; orange red = *calcium*; crimson = *strontium, lithium*; lavender = *potassium, rubidium, cæsium*; apple green = *barium*; bright green = *thallium, copper, boric acid*; pale blue = *lead, antimony*; deep blue becoming green = *copper halides*; deep blue = *selenium.*

The pocket spectroscope (direct vision) is a useful aid in examining flame colourations, particularly in the case of strontium and calcium, which exhibit respectively a characteristic blue and a yellowish-green line.

(4) *Heating on charcoal.*—The substance mixed with three times its weight of dry sodium carbonate or of a mixture of 2 parts sodium carbonate and 1 part potassium cyanide, is placed in a small shallow hole scooped out in charcoal, and heated in a reducing flame. The metallic bead obtained is examined as to colour, malleability, solubility, &c. Many metals yield films of oxide, which coat the charcoal at a greater or less distance from the flame, and the colour and appearance of which are more or less characteristic. These and similar films are best seen when the charcoal is supported on an aluminium plate (Ross). A piece of sheet aluminium 12 cm. by 5 cm. is bent in right angles at a distance of 2 cm. from one end, thus forming a ledge on which a small flat piece of charcoal is placed, the plate being held so that the surface rises vertically behind the ledge. Volatile oxides, &c., condense on the metallic surface (*v.* Hutchings, Chem. News, 1877, 36, 208, 217).

The reduction may also be effected by adding a fragment of sodium to the substance supported on charcoal (Parsons, J. Amer. Chem. Soc. 1901, 23, 159).

In order to obtain reduced metals with the bunsen flame, a match-stick is smeared with ordinary sodium carbonate (washing soda) which has been melted by holding it in the flame, and the wood thus prepared is carbonised by heating it in the flame. A small quantity of the substance is mixed in the palm of the hand with a small quantity of the fused washing soda, and the mixture is carefully placed on the charcoal splint, which is then heated in the lower or upper reducing flame. When reducting is complete, the match is allowed to cool inside the dark zone, and is then withdrawn, crushed in a mortar, and the lighter particles of charcoal removed by levigation with water, the heavy metallic particles being left.

By means of the bunsen flame reduced metals and their oxides can be obtained in the form of films on a porcelain surface. The substance is supported on a long slender piece of asbestos, and heated in the tip of a small oxidising or reducing flame, a small evaporating dish containing cold water being held momentarily just above the asbestos (*v.* Bunsen's Flammenreactionen, Heidelberg, 1880).

Incrustations on charcoal: white, very volatile = *arsenic*; white, less volatile = *antimony*; orange-yellow hot, pale yellow cold = *bismuth*; pale yellow hot, deep yellow cold, white edge = *lead*; yellow hot, white cold = *zinc, molybdenum*; reddish-brown or orange-yellow cold = *cadmium.*

Metallic beads or residues on charcoal: white malleable = *silver, tin, lead*; red malleable = *copper*; grey brittle = *antimony, bismuth*; grey powder, magnetic = *iron, cobalt, nickel*; non-magnetic = *molybdenum.*

(5) *Cobalt nitrate reactions.*—Certain *infusible* substances, when moistened with cobalt nitrate solution and strongly heated, acquire characteristic colours. These reactions are frequently, but not necessarily, carried out on a charcoal support:—blue infusible mass = *aluminium*; blue fusible = *certain phosphates, silicates, borates*; green = *zinc, titanium, tin*; pink = *magnesium.*

(6) *Heating with borax or microcosmic salt.*—A small loop is made at the end of a platinum wire, to which some borax or microcosmic salt is made to adhere, and heated in the flame until fused. The bead when cold must be quite transparent and colourless, otherwise it must be remelted, shaken off, and a fresh bead made. A *small* quantity of the substance is taken on the bead and heated first in the oxidising flame (O.F.) and then, after it has been examined, in the inner or reducing flame (I.F.). The colour of the bead should be observed both hot and cold. If too much substance is taken, the bead becomes opaque, and the colour cannot be distinguished.

These so-called borax and microcosmic beads owe their colour respectively to the formation of certain borates and phosphates of the heavy metals. Borax glass consists of anhydrous $Na_2B_4O_7$, and when heated with a metallic oxide or salt the excess of boric oxide present unites with the metallic oxide, forming the corresponding borate:

$$Na_2B_4O_7+CoO = Na_2B_2O_4+CoB_2O_4 \text{ (blue).}$$

Microcosmic salt on ignition yields the readily fusible sodium metaphosphate, and this salt combines with metallic oxides to form double orthophosphates:

$$NaPO_3+CuO = CuNaPO_4 \text{ (green).}$$

When a silicate is introduced into the molten metaphosphate, the latter withdraws the basic oxide from the former, setting free silica, which remains undissolved ('silica skeleton'):

$$CaSiO_3+NaPO_3 = CaNaPO_4+SiO_2.$$

Borax beads.—

Inner flame		Outer flame		Metal
Hot	Cold	Hot	Cold	
Green	Bottle-green	Yellow	Paler	*Iron*
Green	Green	Yellow	Green	*Chromium*
Green	Bottle-green	Yellow	Pale yellow	*Uranium*
Colourless	Colourless	Amethyst	Amethyst	*Manganese*
Blue	Blue	Blue	Blue	*Cobalt*
Grey	Grey	Violet	Reddish-brown	*Nickel*
Brownish	Emerald-green	Yellow	Greenish-yellow	*Vanadium*
Colourless	Brown	Green	Bluish-green	*Copper*
Colourless	Colourless	Orange-red	Colourless	*Cerium*
Brown	Brown	Yellow	Colourless	*Molybdenum*
Brownish-violet		Yellow	Colourless	*Titanium*
Yellow to brown		Yellow	Colourless	*Tungsten*

Microcosmic beads.—The colours produced are similar to those in the borax bead, but the reducing effects are less pronounced. In the I.F. molybdenum compounds give a green colour, and those of tungsten a greenish-blue tint. Chlorides and bromides evolve a blue and green flame when heated with a microcosmic bead saturated with copper oxide, and iodides give a green flame.

(7) *Other special dry tests.*—(*a*) Heating on charcoal with potassium (or cuprous) iodide and sulphur: crimson incrustation = *bismuth*; lemon yellow incrustation = *lead*; greenish-blue fumes = *mercury.*

(*b*) Heating on charcoal with (i.) fusion mixture (Na_2CO_3,K_2CO_3) alone and moistening with dilute acid, hydrogen sulphide evolved = *sulphur compounds*; (ii.) fusion mixture and sulphur, soluble mass giving coloured precipitate with dilute acid, yellow = *tin*; orange = *antimony.* The fused insoluble oxides SnO_2 and Sb_2O_4 can be thus characterised.

(*c*) Heating with fusion mixture and potassium nitrate: soluble green mass = *manganese*; yellow mass = *chromium.*

(*d*) Heating in closed tube with potassium hydrogen sulphate. Gas evolved: carbon dioxide = *carbonates, oxalates*; accompanied by charring of the residue = *tartrates, citrates,* &c.; carbon monoxide (blue flame) = *formates, oxalates*; sulphur dioxide = *sulphites, thiosulphates*; hydrogen sulphide = *sulphides* (not all); hydrogen chloride (fuming in air) = *chlorides* (not all); hydrogen fluoride (etching glass) = *fluorides*; bromine and hydrogen bromide = *bromides*; iodine = *iodides*; nitrous fumes = *nitrites, nitrates.*

Examination in the Wet Way.

The preparation of the solution requires some attention. A metallic substance is treated at once with moderately strong nitric acid. Tin and antimony form oxides which to a great extent remain undissolved; arsenic is oxidised to soluble arsenic acid; other metals (with the exception of gold and the platinum metals, which are not attacked) are converted into nitrates, which dissolve at once or on diluting.

If the substance is not a metal, it is first treated with hot water, and if anything is dissolved (which is ascertained by evaporating a few drops on platinum foil), the substance is boiled two or three times with fresh quantities of water. Any residue which may be left is treated with dilute hydrochloric acid, and afterwards, if necessary, with the concentrated acid. Care must be taken to observe if any gas is given off—*e.g.* carbon dioxide (effervescence), from *carbonates*; sulphur dioxide, from *sulphites* or *thiosulphates*; chlorine, from *peroxides* or *hypochlorites*; hydrocyanic acid, from *cyanides*; hydrogen sulphide, from *sulphides*. Many chlorides are insoluble in the strong acid, and hence the solution must be diluted before filtering. Silver, lead, and univalent mercury will be converted into insoluble chlorides.

Solvent action of the mineral acids (*v.* A. A. Noyes and W. C. Bray, J. Amer. Chem. Soc. 1907, 29, 137, 481).—In dealing with substances insoluble in water the following acidic solvents may be used: hydrochloric, nitric, sulphuric, and hydrofluoric acids. Although it is impossible to give a hard-and-fast rule as to the way in which these agents should be applied, the following considerations will indicate the relative advantages of one or other of these solvents:—

Hydrochloric acid.—(1) Advantages: (i.) Solutions on this acid do not yield a precipitate of sulphur on treatment with hydrogen sulphide; (ii.) the solvent action of this acid on the following oxides: lead peroxide, manganese dioxide, and the hydrated oxides of tin and antimony, is superior to that of nitric acid; (iii.) hydrated silica is readily precipitated on evaporating the hydrochloric acid solution.

(2) Disadvantages: (i.) This acid is comparatively useless for alloys; (ii.) evaporation of the hydrochloric acid solution leads to the volatilisation of arsenic, mercury, tin and selenium as chlorides.

Nitric acid.—(1) Advantages: (i.) The best general solvent for the metals and their alloys; (ii.) oxidises and dissolves insoluble compounds of arsenic, mercury, and selenium without the formation of volatile compounds of these elements; (iii.) does not cause the precipitation of silver or lead; (iv.) oxidises sulphides not attacked by hydrochloric and sulphuric acids.

(2) Disadvantages: (i.) This acid alters the state of combination of many elements, *e.g.* it oxidises mercurous, arsenious, antimonious, stannous, and ferrous salts; (ii.) its solution deposits much sulphur on treatment with hydrogen sulphide; (iii.) the oxidation of sulphides by nitric acid in the presence of barium, strontium, and lead leads to the precipitation of these metals as sulphates; (iv.) nitric acid is less efficacious than hydrochloric acid in rendering hydrated silica insoluble.

The nitric acid solution of an alloy when evaporated to dryness and heated at 120°-130° may yield the partially dehydrated hydroxides of silica, tin, antimony, titanium, and tungsten in an insoluble condition. When phosphorus or arsenic is present together with tin the so-called stannic phosphate or arsenate (phosphostannic or arsenostannic acid) may also be found in the insoluble residue.

Sulphuric acid.—The dilute acid is of little value as a solvent, but the hot concentrated acid has been found useful in certain cases. (i.) In bringing certain alloys into solution, *e.g.* white metals (*v.* Low, J. Amer. Chem. Soc. 1907, 29, 66); (ii.) destruction of organic matter; evaporation of a concentrated sulphuric acid solution of the substance is preferable to ignition, because the latter process renders certain compounds insoluble and leads to the loss by volatilisation of such elements as mercury, arsenic, selenium, &c. Very stable organic substances (*e.g.* paraffin and cellulose) can be destroyed completely by adding a little strong nitric acid and heating till the solution acquires a light yellow colour. When diluted considerably with water (20–30 vols.) this solution may yield a deposit containing silica and certain refractory silicates and fluosilicates, together with the sulphates of barium, strontium, lead, calcium, and chromium (an insoluble sulphate formed during the heating), basic sulphates of bismuth, antimony, and tin and the ignited oxides of the last two metals with those of aluminium and titanium. (iii.) Insoluble compound cyanides are decomposed by hot concentrated sulphuric acid, but may also be attacked by aqueous alkali hydroxides yielding soluble alkali cyanides and insoluble metallic hydroxides.

Hydrofluoric acid.—The insoluble residues from the preceding acids may be treated with a 40 p.c. solution of hydrogen fluoride, which is now obtainable in glass bottles lined with paraffin wax. (1) Advantages: (i.) Many insoluble silicates are readily decomposed, the silicon being eliminated completely as gaseous silicon fluoride; (ii.) the reducible metals and their compounds may be treated in platinum basins or crucibles providing that the solution is never evaporated to dryness.

(2) Disadvantages: (i.) Glass or silica-ware vessels cannot be used with hydrofluoric acid; (ii.) owing to the destructive action of hydrogen fluoride on animal tissues, all operations with solutions of this gas must be conducted in an efficient draught cupboard.

Aqua regia (concentrated hydrochloric acid 3 parts and nitric acid 1 part) may be employed in attacking substances not dissolved by hydrochloric or nitric acid, although it is of little use for colourless insolubles. It readily dissolves gold and platinum, but is less efficacious in rendering soluble the rarer noble metals (*e.g.* osmium and iridium).

Treatment of Insolubles.

The substances not dissolved by the foregoing acidic reagents are generally regarded as insolubles, although they are divisible into two classes: (i.) *pseudo-insolubles*, which are dissolved by certain specific solvents; (ii.) *true insolubles*, which are only broken up into soluble compounds by the agency of fused alkali carbonates.

Pseudo-insolubles.—*Silver chloride* and *bromide*, soluble in aqueous ammonia. (The three silver halides may be completely decomposed by treatment with zinc and dilute sulphuric acid, metallic silver and soluble zinc halide being produced.) *Insoluble fluorides* (those of the common and rare earth metals) are decomposed by heating with concentrated sulphuric acid. *Lead sulphate*, soluble in ammonium acetate solution; *oxides of antimony*, dissolved in hydrochloric and tartaric acids. *Anhydrous chromic sulphate* and *basic bismuth sulphate*, converted respectively into hydroxide and basic carbonate by boiling with aqueous sodium carbonate; these products are then dissolved in dilute mineral acids.

True insolubles.—These substances are fused with a mixture of sodium and potassium carbonates in equimolecular proportions (so-called fusion mixture). In the absence of reducible metals (*e.g.* silver or lead), insoluble sulphates (barium and strontium sulphates) and silicates may be heated with the fusion mixture in a platinum crucible. If any insoluble molybdenum sulphide is present (indicated by dry tests), a little nitre must be added to oxidise this sulphide, and thus prevent its corrosive action on the platinum. In the case of an insoluble silicate the fused mass is treated directly with hydrochloric acid, when the metals present pass into solution as chlorides, and the silica is rendered insoluble by evaporating down the acid solution. In the case of insoluble sulphates the fused mass is extracted with water to remove the soluble alkali sulphate, and the residue ($BaCO_3$,$SrCO_3$) is subsequently dissolved in dilute acid.

Silver iodide, bromide, and chloride are decomposed by 'fusion mixture,' yielding the soluble alkali halide; insoluble lead compounds are similarly decomposed. The strongly heated oxides of aluminium, chromium, titanium, tin, and antimony rank as insolubles; they are not readily attacked by 'fusion mixture,' but are rendered soluble by fusion with potassium hydroxide. The oxides of titanium and aluminium may be rendered soluble by fusion with potassium hydrogen sulphate; special methods for treating the insoluble oxides of chromium, tin, and antimony are indicated among the dry tests (7, *b* and *c*). The insoluble compounds of the easily reducible metals (*e.g.* Ag, Pb, Sn, Sb, &c.) can all be decomposed and reduced by fusion with sodium or potassium cyanide.

When both aqueous and acid solutions have been obtained from the same substance, the analyst must use his judgment as to whether they may be mixed or should be analysed separately. The latter course sometimes gives information as to the distribution of the acids and bases in the original substance. If the first course is adopted, it must be borne in mind that the hydrochloric acid solution may precipitate lead and silver, and possibly mercury, from an aqueous or nitric acid solution.

Systematic Method of Examination in the Wet Way.

The formation of a precipitate at the proper stage in the systematic separation is not sufficient proof of the presence of a particular substance; some characteristic confirmatory test should always be applied. The colour of the solutions at different stages in the operation is a valuable indication. Unnecessary excess of reagents should be avoided, but filtrates should always be tested to make sure that precipitation is complete. Many tests succeed only when the proper proportion of the reagent is added, and it should be a rule always to add the reagents very gradually. All precipitates which have to be subjected to the action of reagents should be carefully washed, but in qualitative analysis it is not as a rule desirable that all the washings should mix with the filtrate.

The reaction of the original solution towards litmus paper should be noted and a portion tested for ammonium compounds by heating with sodium hydroxide or by triturating in a mortar with soda-lime (dry sodium and calcium hydroxides).

In systematic qualitative analysis advantage is taken of certain *similarities* existing between the metallic radicals which enable these radicals to be divided into a limited number of groups, the members of which are subsequently either separated or identified by means of the *differences* between the properties of their respective compounds.

The metallic radicals are divided into six groups, according to their behaviour with the following reagents, which must be applied in the order given. It may be mentioned that some chemists prefer a division into five groups, and add the reagents of Groups III. and IV. successively *without* an intervening filtration. This process is conveniently adopted in the presence of the less commonly occurring metals (J. Amer. Chem. Soc. 1908, 30, 481).

Group I.—Reagent: hydrochloric acid in moderate excess. Precipitate: *silver*, *lead*, *thallium* (*thallous*), and *mercurous chlorides*; *tungstic acid*.

If the original solution is alkaline, the group precipitate may contain sulphides (*e.g.* As_2S_3, Sb_2S_3, SnS_2) which had been dissolved in aqueous alkali sulphide or hydroxide. This yellow or orange precipitate is examined under Group II. The group precipitate may also contain insoluble silver salts (*e.g.* AgBr, AgI) precipitated from solution in alkaline cyanides or thiosulphates; these are dealt with as insolubles. The filtrate from the Group I. precipitate or the solution itself in the absence of a precipitate, must be evaporated nearly to dryness if nitric acid or nitrates are present, since these compounds lead to the precipitation of sulphur in Group II.

Group II.—Reagent: hydrogen sulphide in acid solution. Thioacetic acid has been recommended as a substitute for hydrogen sulphide in qualitative analysis (Schiff and Tarugi, Ber. 1894, 27, 2437). Precipitate: the *sulphides* of *arsenic*, *antimony*, *tin*, *molybdenum*, *gold*, *platinum* (*the other platinum metals*), *bismuth*, *lead*, *mercury*, *copper*, and *cadmium*, together with *selenium* and *tellurium*, partly free and partly as *sulphides*. The solution should be dilute and not too acid, and it should be treated and saturated repeatedly with the group reagent, since prolonged treatment is required to precipitate molybdenum and the platinum metals.

The filtrate from the foregoing sulphides is boiled to expel hydrogen sulphide, and any iron present peroxidised by warming with nitric acid or bromine water. If organic matter is present, it is destroyed either by evaporation to dryness or treatment with hot concentrated sulphuric acid (*v. supra*). Silica or barium sulphate may be precipitated at this stage. A portion of the oxidised solution should now be tested for phosphate with nitric acid and ammonium molybdate.

Group III.—Reagents: ammonium chloride and ammonium hydroxide. Precipitate: (*a*) In absence of phosphates: *hydroxides* of *aluminium*, *iron*, *chromium*, *glucinum*, *titanium*, *zirconium*, *tantalum*, *columbium*, *thorium*, *cerium* (*and other rare earth metals*), and *uranium* as *ammonium diuranate*. Some manganese, zinc, and alkaline earth metals may be coprecipitated. (*b*) In presence of phosphates: *the phosphates of the preceding metals, together with those of Groups IV., V., and magnesium.*

Group IV.—Reagents: ammonium sulphide or hydrogen sulphide and ammonium hydroxide. Precipitate: *sulphides* of *zinc, manganese, cobalt, and nickel.* The precipitation is carried out in the boiling solution, and the filtrate, if brown, is slightly acidified with hydrochloric acid, when *vanadium* and a small portion of the nickel are precipitated as sulphides.

Group V.—Reagents. ammonium carbonate and ammonia. Precipitate: *barium, strontium,* and *calcium* as *carbonates.*

Group VI.—The filtrate from Group V. contains *magnesium, sodium, lithium, potassium, rubidium,* and *cæsium,* which are identified by special tests.

In the absence of the rarer metallic radicals, the group precipitates are examined in the following manner. Confirmatory tests are given under special reactions.

Group I.—The precipitate is boiled with water; the aqueous extract mixed with dilute sulphuric acid gives a white precipitate ($PbSO_4$), indicating *lead.* The insoluble portion is treated with aqueous ammonia; a black residue (NH_2Hg_2Cl or NH_2HgCl and Hg) indicates *mercury*; the ammoniacal filtrate acidified with nitric acid gives white silver chloride, indicating *silver.*

Group II.—The precipitate is washed with aqueous hydrogen sulphide and warmed with yellow ammonium sulphide [$(NH_4)_2S_x$], this extraction being repeated.

(A) The filtrate is acidified with dilute hydrochloric acid, the precipitate boiled with strong aqueous ammonium carbonate, and the solution filtered, the filtrate acidified yields a yellow precipitate (As_2S_3), denoting *arsenic.* The residue is dissolved in concentrated hydrochloric acid, the solution boiled, diluted, and treated with strips of platinum and pure zinc; a black stain on the platinum = *antimony.* The zinc is dissolved in hydrochloric acid and mercuric chloride added; a white precipitate (Hg_2Cl_2) becoming grey (Hg) = *tin.*

In the separation of arsenic, antimony, and tin by ammonium carbonate, this solvent dissolves an appreciable amount of stannic sulphide, which is reprecipitated by acids as a white oxysulphide (Schmidt, Ber. 1894, 27, 2739).

Boiling the mixed sulphides with concentrated hydrochloric acid effects a separation by dissolving the tin and antimony compounds, leaving nearly the whole of the arsenious sulphide undissolved. The mixed sulphides may also be dissolved in aqueous sodium peroxide, which produces sodium arsenate, antimonate, and stannate. On boiling this solution with excess of ammonium chloride, hydrated stannic oxide is precipitated (*v.* J. Walker, Chem. Soc. Trans. 1903, 83, 184; *cf.* Cavén, Chem. Soc. Proc. 1910, 26, 176).

(B) The precipitate insoluble in ammonium sulphide is boiled with nitric acid (1 vol. acid sp.gr. 1·20 : 2 vols. H_2O), the residue dissolved in aqua regia, excess of acid expelled, and stannous chloride added; a white precipitate (Hg_2Cl_2) indicates *mercury.* The nitric acid solution is evaporated to a small bulk with sulphuric acid, diluted with cold water and filtered; white residue ($PbSO_4$) indicates *lead.* The filtrate is rendered ammoniacal, blue colour = *copper*; white precipitate ($Bi(HO)_3$) = *bismuth,* confirmed by dissolving in hydrochloric acid and diluting considerably with water (BiOCl). The colour of the filtrate discharged by potassium cyanide (excess); the solution saturated with hydrogen sulphide, a yellow precipitate (CdS) = *cadmium* (confirmation is essential, since a yellow cyanogen derivative may be precipitated at this stage).

Group III. (phosphates absent).—The mixed hydroxides, suspended in water, are warmed with excess of sodium peroxide and filtered. A residue ($Fe_2O_3{\cdot}xH_2O$, which may contain some MnO_2) indicates *iron.* The filtrate is divided into two parts, (i.) boiled with excess of ammonium chloride, white gelatinous precipitate ($Al(OH)_3$) = *aluminium*; (ii.) acidified with dilute acetic acid and lead acetate added, yellow precipitate ($PbCrO_4$) = *chromium.*

Group III. (phosphates present).—If the original solution was acid, this group precipitate may contain phosphates insoluble in neutral or alkaline solutions. The sodium peroxide separation is applied to one-third of the precipitate; the remainder is dissolved in dilute hydrochloric acid, the solution nearly neutralised with pure sodium carbonate, and treated successively with ammonium acetate, acetic acid, and ferric chloride until no further precipitate is produced and the solution is deep red. The mixture is boiled and filtered hot; the filtrate is then examined for the metals of Groups IV. and V., and for magnesium. The precipitate, which is neglected, contains ferric phosphate and basic ferric acetate. Ammonium formate may be used instead of acetate in this separation (Tower, J. Amer. Chem. Soc. 1910, 32, 953).

The phosphoric acid may also be removed by evaporating the filtrate from Group II. to dryness with nitric acid and granulated tin, when an insoluble residue is obtained consisting of metastannic and phosphostannic acids.

Group IV.—The mixed sulphides, washed with hydrogen sulphide water, are dissolved in aqua regia, or hydrochloric acid and potassium chlorate. Excess of sodium hydroxide is added to the solution after expelling excess of acid; the precipitate collected and the filtrate treated with hydrogen sulphide; white precipitate (ZnS) = *zinc.* The precipitated hydroxides are dissolved in hydrochloric acid, excess of ammonium acetate added, and the solution saturated with sulphide. Any black precipitate is removed and the filtrate rendered ammoniacal; pink precipitate (MnS) = *manganese.*

The black precipitate is tested in the borax bead; a brownish-yellow colour indicates *nickel* present and cobalt absent. If the bead is blue (= *cobalt*), the precipitate is dissolved in hydrochloric acid, potassium chlorate added, excess of acid expelled, and the solution *nearly* neutralised with sodium carbonate; excess of potassium cyanide is then added, and the solution boiled in an open dish. An excess of sodium hypochlorite or freshly prepared sodium hypobromite is added to the warm solution; a black precipitate (Ni_2O_3,xH_2O) = *nickel*;

the filtrate contains potassium cobalticyanide ($K_3Co(CN)_6$).

A quicker separation of the Group IV. sulphides may be effected by digesting them with cold dilute hydrochloric acid (1 : 20). This treatment should bring the zinc and manganese into solution, leaving the sulphides of nickel and cobalt undissolved; but it is generally found that appreciable quantities of the latter metals are present in the filtrate. Alternative methods of detecting and separating nickel and cobalt are given under special reactions.

Group V.—Dissolve the washed precipitate in dilute acetic acid, add aqueous potassium chromate; yellow precipitate ($BaCrO_4$) = *barium*: filtrate boiled with concentrated aqueous ammonium sulphate; white precipitate ($SrSO_4$) = *strontium*: final filtrate treated with ammonium oxalate; white precipitate (CaC_2O_4,xH_2O) = *calcium*. Owing to their close relationship, a sharp separation of the three metals is extremely difficult. The following alternative process has been worked out (*v.* Bray, J. Amer. Chem. Soc. 1909, 31, 611).

The group precipitate, which may contain magnesium, is dissolved in 20 c.c. of 30 p.c. acetic acid, solution neutralised with ammonia, 3 c.c. of acetic acid added, diluted to 40 c.c., 10 c.c. of 20 p.c. potassium chromate slowly added, solution boiled for 2 minutes; yellow precipitate ($BaCrO_4$). Three c.c. of ammonia added to filtrate, diluted to 60 c.c., 50 c.c. of alcohol (95 p.c.) added; after 10 minutes yellow precipitate ($SrCrO_4$). Without washing this precipitate, 200 c.c. of water are added to filtrate, the solution boiled, and 40 c.c. of 4 p.c. ammonium oxalate added; after 10 minutes white precipitate (CaC_2O_4). *Magnesium* is precipitated in filtrate as a colourless crystalline precipitate ($Mg(NH_4)PO_4,6H_2O$) by adding ammonia and sodium phosphate.

Group VI.—A portion of the filtrate from V. examined for *magnesium* (*v. supra*), the remainder evaporated to dryness and ignited to expel ammonium salts. The residue dissolved in a small bulk of water, the solution filtered if necessary, examined by flame test and divided into two parts, (i.) platinic chloride added; yellow crystalline precipitate (K_2PtCl_6) = *potassium*; (ii.) potassium pyroantimonate added; colourless crystalline precipitate ($Na_2H_2Sb_2O_7,6H_2O$) = *sodium*.

Group Separation in the Presence of the Rarer Metals.

In the presence of the less commonly occurring elements, the ordinary group separations require, in certain instances, to be modified very considerably. A systematic attempt to deal with this problem has recently been made by A. A. Noyes and his collaborators, to whose original memoirs reference should be made for the exact working details of the necessarily somewhat complicated separations, an outline of which is given below (J. Amer. Chem. Soc. 1907, 29, 137; 1908, 30, 481; 1909, 31, 611).

It will be seen that the greater number of the rarer elements are precipitated by the reagents of Groups II., III., and IV. of the foregoing analytical classification; but in the scheme devised by Noyes, Groups III. and IV. are merged into one, and it is chiefly in this comprehensive group that the additional complications are to be found.

Group I.—The precipitate may contain *thallous chloride* and *tungstic acid*. The former is extracted by hot water, any lead separated as sulphate, when the filtrate treated with potassium iodide gives a yellow precipitate (TlI) = *thallium*. The hydrated tungstic acid, precipitated by hydrochloric acid from alkali tungstates, remains in the residue, and may be separated from lead and silver by fusion with sodium carbonate. The aqueous solution of alkali tungstate is boiled with zinc and hydrochloric acid, when the development of a blue colouration = *tungsten*.

Group II.—Selenium, tellurium, molybdenum, gold, platinum and its allies, are precipitated by hydrogen sulphide in acid solution. Extraction of the group precipitate with yellow ammonium sulphide carries the greater part of these elements into the tin sub-group, but the separation is not quite sharp, for small but appreciable quantities of molybdenum, gold and the platinum metals remain in the insoluble sulphides of the copper sub-group.

A. *Copper sub-group.*—The precipitate boiled with dilute nitric acid (1 vol. of sp.gr. 1·20 : 2 vols. water) partially dissolves; the solution contains lead, copper, cadmium, and bismuth, while the residue contains mercury, gold, platinum, and a trace of tin. The insoluble portion is oxidised with bromine water, potassium chloride and hydrochloric acid are added and the solution concentrated; a yellow crystalline precipitate (K_2PtCl_6) = *platinum*. The excess of acid is expelled from the solution, which is then rendered alkaline and boiled with excess of oxalic acid; a brownish-black precipitate = *gold*.

B. *Tin sub-group.*—The sulphides are reprecipitated by dilute acid from their solution in ammonium sulphide, and digested for 10 minutes with nearly boiling hydrochloric acid (sp.gr. 1·20); the solution contains tin and antimony, and the residue arsenic and the rarer elements. The residue is dissolved by strong hydrochloric acid and potassium chlorate; the solution concentrated to the crystallising point yields a yellow precipitate (K_2PtCl_6)=*platinum*. The filtrate, treated successively with ammonia and magnesia mixture ($MgCl_2,2NH_4Cl$ with $NH_4{\cdot}OH$), yields a colourless crystalline precipitate ($Mg(NH_4)AsO_4,6H_2O$) = *arsenic*. The filtrate from the double arsenate is evaporated to remove ammonia, and then boiled with oxalic acid, and the brownish-black precipitate (*gold*) extracted with hydrochloric acid to dissolve any co-precipitated tellurous acid. The filtrate from the gold is concentrated and acidified with strong hydrochloric acid, and after removing any precipitated potassium chloride, sodium sulphite (in *slight* excess) is added when a red precipitate = *selenium*. The filtrate from selenium is diluted and treated successively with potassium iodide and solid sodium sulphite (excess); the double iodide, K_2TeI_6, becomes reduced, and a black precipitate = *tellurium*. The final filtrate is boiled with hydrochloric acid to expel sulphur dioxide, and to the cooled solution 10 p.c. potassium thiocyanate and stannous chloride (or a scrap of zinc) are successively added, when a red colouration ($MO(CNS)_4$) soluble in ether = *molybdenum*.

GROUPS III. and IV.—The filtrate from Group II. is boiled to expel hydrogen sulphide, treated with moderately strong ammonia, the colour of the precipitate being noted, and the ammoniacal mixture heated nearly to boiling and treated with ammonium sulphide, or preferably, in the presence of nickel, with hydrogen sulphide to saturation. In the presence of vanadium the filtrate has a reddish colour, and on adding hydrochloric acid brown vanadium sulphide is precipitated. The acid filtrate is boiled to expel hydrogen sulphide, and treated with ferric chloride and ammonia to precipitate last traces of vanadium. The presence of this metal in the sulphide and ferric hydroxide precipitates is confirmed by dissolving in nitric acid (sp.gr. 1·20), diluting and adding hydrogen peroxide, when an orange-yellow colouration = *vanadium*.

The group precipitate is dissolved in hydrochloric acid (sp.gr. 1·12), adding, if necessary, some nitric acid or bromine water. The solution is then boiled with hydrochloric acid to remove nitric acid, and treated in a platinum dish with 40 p.c. hydrofluoric acid, and evaporated to dryness. An insoluble residue indicates the fluorides of the rare earth metals (thorium, cerium, yttrium, erbium, &c.); the aqueous extract, which contains all the other metals of this analytical group, is evaporated successively with hydrochloric and nitric acids. The insoluble fluorides are decomposed by hot sulphuric acid, and the resulting sulphates of the rare earth metals subjected to special tests for these elements.

The nitric acid solution of the other metals of the group is treated successively with caustic soda solution, dry sodium peroxide, and aqueous sodium carbonate, when a precipitate B and a filtrate A are obtained. This treatment separates these metals into two sub-groups, and the method is valid even when phosphates are present.

A. *The aluminium sub-group* (may contain sodium glucinate, zincate, aluminate, vanadate, chromate, and peruranate). The solution is acidified with nitric acid (sp.gr. 1·42) and diluted considerably, solid sodium hydrogen carbonate added in moderate excess and the mixture heated in a stoppered bottle. The precipitate (containing zinc, glucinum, and aluminium) is dissolved in hydrochloric acid, and the solution rendered ammoniacal; the zinc remains in solution, while the hydroxides of glucinum and aluminium are precipitated. These hydroxides are dissolved in strong hydrochloric acid, ether (1·5 vols.) is added, and the cooled solution saturated with hydrogen chloride, white crystalline precipitate ($AlCl_3,6H_2O$) = *aluminium*. The ethereal filtrate is evaporated, treated with ammonia, any precipitate dissolved in 10 p.c. sodium hydrogen carbonate, the solution saturated with hydrogen sulphide; the filtrate from any precipitated sulphide is acidified, boiled, and rendered ammoniacal, when a white flocculent precipitate ($Gl(OH)_2$) = *glucinum*.

The filtrate obtained from the first treatment with sodium hydrogen carbonate is acidified with nitric acid, and just neutralised with caustic soda; 2 c.c. of nitric acid (sp.gr. 1·20 and 20 c.c. of 20 p.c. lead nitrate are added; yellow precipitate = *chromium*. The lead is removed with hydrogen sulphide, the excess of gas boiled off, vanadyl salts oxidised to vanadates with bromine, any excess of this reagent being removed by boiling. The solution, after neutralisation with ammonia, is treated successively with 5 c.c. of 30 p.c. acetic acid, 2 grams of ammonium sulphate (or nitrate), and 2 grams of sodium phosphate; the mixture is heated to boiling, when a white precipitate ($UO_2(NH_4)PO_4$) = *uranium*. The final filtrate is rendered ammoniacal, saturated with hydrogen sulphide, acidified with acetic acid, and boiled; dark precipitate = *vanadium*.

B. *The iron-manganese sub-group* (may contain the hydroxides and phosphates of iron, manganese, cobalt, nickel, zinc (traces), titanium, and zirconium, together with calcium, strontium, barium, and magnesium, as carbonates and phosphates). The precipitated hydroxides, &c., are dissolved in hydrochloric acid, the solution evaporated down with strong nitric acid, and treated with 0·5 gram of solid potassium chlorate; brown precipitate = *manganese*. A portion of the filtrate tested for phosphoric acid, when, if present, the remainder is treated with ammonium hydroxide till nearly alkaline, and boiled with ferric chloride and ammonium acetate. The filtrate contains the ordinary metals of Groups III. and IV., together with magnesium; the precipitate consists of the hydroxides, phosphates, and basic acetates of iron, zirconium, titanium, and possibly thallium (tervalent). This precipitate is dissolved in hydrochloric acid (sp.gr. 1·12), and the solution shaken with an equal volume of ether. The ethereal extract contains ferric and thallic chlorides; the hydrochloric acid solution the zirconium and titanium. The latter is evaporated down with sulphuric acid until the hydrogen chloride is expelled, the residue taken up with water and treated with hydrogen peroxide and subsequently with sodium phosphate; orange-yellow colouration (TiO_3) = *titanium*; white flocculent precipitate ($Zr(OH){\cdot}PO_4$) = *zirconium*. The final filtrate is reduced with sulphurous acid, when a white flocculent precipitate ($Ti(OH){\cdot}PO_4$) confirms *titanium*.

GROUPS V. and VI.—In the presence of lithium it is preferable to precipitate magnesium in the calcium group. The filtrate from Groups III. and IV. is concentrated to 10 c.c. and treated with 30 c.c. of 20 p.c. ammonium carbonate and 30 c.c. of 95 p.c. alcohol. After 30 minutes the precipitation is complete, the magnesium being present as the double carbonate ($MgCO_3,(NH_4)_2CO_3,4H_2O$). The treatment of the group precipitate has already been described under Group V. (*v. supra*). The filtrate is evaporated to dryness and ignited. The residue is taken up with 10 c.c. of water, and one-third tested for lithium by adding 0·5 c.c. of 10 p.c. caustic soda and 2 c.c. of 10 p.c. sodium phosphate, heating to boiling and adding 1 c.c. of alcohol, white precipitate (Li_3PO_4) = *lithium*. The filtrate from this phosphate is tested for potassium by adding acetic acid and sodium cobaltinitrite. The remaining two-thirds of the solution, containing the alkali metals, are tested for sodium by potassium pyroantimonate after removing the lithium as fluoride by ammonia and ammonium fluoride.

Examination for Acids.

Although it is not possible to separate the acidic radicals into a limited number of groups, each having a group reagent, yet the reactions may be divided into (i.) preliminary tests made on the original solution or substance; and (ii.) systematic tests made on suitably prepared solutions. The reactions may be conveniently carried out in the following order:—

I. *Preliminary tests* (compare dry reactions).

1. The original substance or solution is warmed with dilute hydrochloric or sulphuric acid. A gas is evolved, carbon dioxide, turning lime water milky = *carbonate*; sulphur dioxide = *sulphite*; hydrogen sulphide, blackening lead acetate paper = *sulphide* (not all); nitrous fumes = *nitrite*; hydrogen cyanide, odour of bitter almonds = *cyanide*.

2. The original substance or solution warmed slowly with strong solution of sodium dichromate slightly acidified, carbon dioxide evolved, confirms *carbonate* in presence of sulphite.

3. *Heating with concentrated sulphuric acid.*—The foregoing gases may be evolved, and in addition the following:—

(*a*) *Colourless*:

Fuming acid gas etching glass = *fluoride*; fuming acid gas not etching = *chloride*; odour of vinegar = *acetate*; carbon monoxide, blue flame = *formate, ferrocyanide*; carbon monoxide and dioxide = *oxalate*; sulphur dioxide and sulphur sublimate = *thiosulphate*.

(*b*) *Colour*.

Orange vapour, bromine = *bromide*; violet vapour and hydrogen sulphide = *iodide*; nitrous fumes = *nitrite, nitrate*; oxides of carbon and sulphur with charring = *tartrate, citrate, malate*; yellow explosive chlorine oxide = *chlorate*.

4. *Heating with alcohol and concentrated sulphuric acid*, green flame = *borate*. Before performing this test chlorates must be decomposed by igniting the original substance, otherwise an explosion may result.

5. *Heating with concentrated sulphuric acid and sand*, a colourless gas (SiF_4), giving a gelatinous precipitate on moist rod, confirms *fluoride*.

II. *Systematic tests.*—Before testing a solution for acids, boil with excess of pure sodium carbonate to remove heavy metals, filter, and carefully neutralise with nitric acid.

1. *Barium chloride* in neutral solution yields: (*a*) a white precipitate, insoluble in hydrochloric acid = *sulphate, silicofluoride*; (*β*) a white precipitate, soluble in hydrochloric acid = *sulphite, carbonate, phosphate, oxalate, borate, fluoride, silicate, tartrate*; (*γ*) a yellow precipitate = *chromate*.

2. To a portion of the neutral solution add *calcium chloride* in excess, allow to stand for some time with occasional shaking, and filter. A white precipitate (*a*) insoluble in acetic acid = *oxalate* (*sulphate* in strong solutions); (*β*) soluble in acetic acid = *phosphate, borate*, and other acids precipitated by barium chloride.

Calcium *tartrate* after washing is soluble in potash, and is re-precipitated on diluting and boiling.

The filtrate from the precipitate in the cold is boiled for some time and filtered hot; a white precipitate = *citrate* (*malate* in strong solutions). The filtrate from this precipitate is allowed to cool and then mixed with excess of alcohol; a white precipitate = *succinate, malate*.

3. *Silver nitrate* in neutral solution yields:

(*a*) A precipitate soluble in nitric acid.

(1) White = *oxalate, borate, tartrate, benzoate*, &c.

(2) Yellow = *phosphate, arsenite*.

(3) Brick-red = *arsenate*.

(4) Dark-red = *chromate*.

(*β*) A precipitate insoluble in nitric acid.

Soluble in ammonia: White = *chloride* (*hypochlorite*), *cyanide, thiocyanate*; yellowish-white = *bromide*; orange-red = *ferricyanide*; white = *ferrocyanide* (sparingly soluble).

Insoluble in ammonia: Yellow = *iodide* black = *sulphide*.

4. *Ferric chloride* in neutral solutions yields:

(*a*) A colouration: blood-red = *acetate, formate* (precipitate on boiling), *thiocyanate* (no precipitate on boiling); violet = *salicylate, thiosulphate* (fugitive); bluish-black = *tannate, gallate*; greenish-brown = *ferricyanide* (dark-blue precipitate on adding stannous chloride).

(*β*) A precipitate: buff = *benzoate, carbonate*; reddish-brown = *succinate*; white = *phosphate*; black = *sulphide*; bluish- or greenish-black = *tannate, gallate*.

Sulphur acids. (1) Detect *sulphate* by barium chloride, and *sulphide* by lead acetate, &c. Make part of the solution slightly alkaline with potash, add zinc sulphate in considerable excess, and filter. Test one part of the filtrate for *thiosulphate* by means of hydrochloric acid; to the other part add acetic acid till *faintly* acid, sodium nitroprusside in small quantity, and potassium ferrocyanide; a pink precipitate indicates a *sulphite*.

(2) Separation of soluble sulphates, sulphites, sulphides, and thiosulphates in neutral solution. Precipitate *sulphide* as CdS, PbS, or ZnS by adding cadmium carbonate or lead carbonate sludge or zinc chloride solution. Add strontium nitrate and leave for 12 hours; the precipitated strontium *sulphate* and *sulphite* separated by hydrochloric acid, the filtrate contains the *thiosulphate*, decomposed by strong hydrochloric acid, giving sulphur and sulphur dioxide (Autenrieth and Windaus, Zeitsch. anal. Chem. 1898, 37, 295).

Chloride, bromide, and iodide. (1) Place the substance in a small flask connected with a small bulb U-tube containing a little starch paste and placed in a beaker of water. Add water and ferric sulphate solution to the substance in the flask, and heat to boiling. If iodine is present, the starch paste becomes blue. Remove the cork, boil with fresh additions of ferric sulphate till all iodine is expelled. Now add a few crystals of potassium permanganate, connect with a bulb tube containing chloroform, and again boil. If bromine is present, the chloroform is coloured brown. Boil with addition of more permanganate until all bromine is expelled, filter and test filtrate for chlorine (Hart, Amer. Chem. J. 1884, 6, 346).

(2) After iodine has been detected by means of nitrogen oxides in sulphuric acid, evaporate part of the solution to dryness with sodium

carbonate, fuse with ten times its weight of potassium dichromate till all iodine is expelled, place in a small dry retort, and heat with strong sulphuric acid. Part of the distillate is agitated with water and carbon disulphide; if bromine is present, the latter becomes orange-red. The remainder of the distillate is neutralised with ammonia, and tested for chromic acid by acidifying with acetic acid and adding lead acetate. The presence of chromic acid indicates the presence of chlorine in the original substance.

(3) A neutral solution of the three halides is treated with potassium iodate and dilute acetic acid; as iodine is liberated, more iodate is added and the solution boiled until all the iodine is eliminated. The solution is mixed with half its volume of $5N$-nitric acid, bromine is evolved and the solution boiled till colourless A little potassium iodide added to destroy the iodate in excess, and the solution boiled till colourless, then an equal volume of strong nitric acid and a few drops of silver nitrate are added, when a white precipitate indicates a chloride: The strong nitric acid holds in solution any trace of silver iodate. If thiocyanic acid is present, the test for iodine must be made in a small portion of the original solution, adding sodium acetate as well as acetic acid to depress the dissociation of the latter (Benedikt and Snell, J. Amer. Chem. Soc. 1903, 25, 809).

Other acids must be detected by special tests. Iodine, and ferrocyanides and ferricyanides must be removed before testing for nitrates.

To remove iodine, ferrocyanic, ferricyanic, and thiocyanic acids, add excess of a mixture of cupric and ferrous sulphates, and filter. To remove excess of copper and iron (which is not always necessary) heat to boiling, add slight excess of *pure* caustic potash or soda, and filter.

To remove bromine and iodine, acidify with dilute sulphuric acid, and boil with successive additions of potassium permanganate until the liquid has a faint permanent pink tinge; filter.

To remove hypochlorous and nitrous acids, acidify with dilute sulphuric acid, and boil. Nitrous acid can also be decomposed by boiling with a strong solution of ammonium chloride.

For an alternative classification of the acidic radicals into analytical groups, compare T. Milobendski (J. Russ. Phys. Chem. Soc. 1909, 41, 1301).

SPECIAL REACTIONS.

In the following lists only the most characteristic and useful reactions have been given; negative reactions, and others not particularly characteristic, have, as a rule, been omitted (*see also* Dry reactions).

METALS.

The metals are arranged in the order of their occurrence in the systematic separation.

Silver.

Hydrochloric acid, a white precipitate (AgCl), insoluble in hot water and in nitric acid; soluble in ammonia and reprecipitated by nitric acid in excess. *Potassium chromate*, a dark-red precipitate (Ag_2CrO_4); soluble in mineral acids and decomposed by caustic alkalis. *Potassium cyanide*, white precipitate (AgCN) soluble in excess to $KAg(CN)_2$.

Lead.

Hydrochloric acid, a white precipitate ($PbCl_2$), soluble in hot water, from which it crystallises on cooling; insoluble in ammonia. *Hydrogen sulphide*, a black precipitate (PbS), insoluble in ammonium sulphide (in presence of hydrogen halides, intermediate red compounds are produced, *e.g.* PbS,4PbI_2, J. Amer. Chem. Soc. 1895, 17, 511; 1901, 23, 680); soluble in nitric acid. *Sulphuric acid*, a white precipitate ($PbSO_4$), soluble in hot hydrochloric acid; insoluble in dilute sulphuric acid; soluble in ammonium acetate (Noyes and Whitcomb, J. Amer. Chem. Soc. 1905, 27, 747). *Potassium chromate*, yellow precipitate ($PbCrO_4$), insoluble in acetic acid; soluble in potassium hydroxide.

Thallium.

Hydrochloric acid, white precipitate (TlCl), only slightly soluble in hot water. *Potassium iodide*, pale-yellow precipitate (TlI), even in dilute solutions. *Sulphuric acid*, no precipitate (diff. from Pb). *Sodium cobaltinitrite* gives red crystalline precipitate ($Tl_3Co(NO_2)_6$) (J. Russ. Phys. Chem. Soc. 1910, 42, 94).

Tungsten.

Hydrochloric acid, a yellowish-white precipitate (H_2WO_4), insoluble in excess of the dilute acid; soluble in the concentrated acid and in tartaric acid; fragments of zinc added to this solution produce a blue colouration. *Stannous chloride*, a yellow precipitate, which becomes blue if mixed with hydrochloric acid and heated. *Ammonium sulphide*, no precipitate with sodium tungstate, but on acidifying, light-brown precipitate (WS_3), insoluble in hydrochloric acids, soluble in ammonium sulphide.

Mercury.

Mercurous compounds. Hydrochloric acid, white precipitate (Hg_2Cl_2), insoluble in hot water; insoluble in ammonia, but blackened (NH_2Hg_2Cl). *Stannous chloride*, grey precipitate (Hg). *Metallic copper*, becomes coated with mercury, which can be sublimed.

Mercuric compounds. Hydrogen sulphide, white precipitate, becoming yellow, red, and then black (HgS); insoluble in ammonium sulphide; appreciably soluble in alkali sulphides ($Hg(SNa)_2$), insoluble in nitric acid; soluble in aqua regia. *Stannous chloride*, white precipitate (Hg_2Cl_2), becoming grey (Hg) with excess of the reagent. *Potassium iodide*, scarlet precipitate (HgI_2), soluble in excess. *Metallic copper*, as mercurous salts. For detection of minute traces of mercury, as in toxicological inquiries by electrolytic and spectroscopic methods, *see* Browning (Chem. Soc. Trans. 1917, 111, 236).

Bismuth.

Hydrogen sulphide, brown precipitate (Bi_2S_3), insoluble in ammonium sulphide; soluble in nitric acid. *Ammonia*, white precipitate ($Bi(HO)_3$), soluble in hydrochloric acid. *Water* in large excess (with previous addition of ammonium chloride if chlorides are absent), white precipitate (BiOCl), soluble in hydrochloric acid; insoluble in tartaric acid. *Reducing agents* (sodium stannite, hypophosphites, hydrosulphites, formaldehyde in alkaline solution) reduce bismuth compounds to elemental bismuth.

Copper.

Hydrogen sulphide, black precipitate (CuS), insoluble in ammonium sulphide and in dilute sulphuric acid; soluble in nitric acid and in potassium cyanide. *Ammonia*, blue precipitate, soluble in excess to dark-blue solution. *Potassium ferrocyanide*, chocolate-brown precipitate, insoluble in dilute acids; in very dilute solutions colouration only; decomposed by sodium hydroxide, yielding blue copper hydroxide.

Cadmium.

Hydrogen sulphide, yellow precipitate (CdS), insoluble in ammonium sulphide and potassium cyanide; soluble in nitric acid and hot dilute sulphuric acid. *Ammonia*, white precipitate (CdH_2O_2), readily soluble in excess. *Caustic potash* or *soda*, white precipitate (CdH_2O_2) insoluble in excess. An ammoniacal solution of ammonium perchlorate precipitates white double perchlorate ($Cd(ClO_4)_2{\cdot}4NH_3$).

Tin.

Stannous compounds. Hydrogen sulphide, dark-brown precipitate (SnS), soluble in yellow but not in colourless ammonium sulphide. *Mercuric chloride*, white precipitate (Hg_2Cl_2), becoming grey (Hg).

Stannic compounds. Hydrogen sulphide, yellow precipitate (SnS_2), soluble in ammonium sulphide; appreciably soluble in ammonium carbonate (Ber. 1894, 27, 2739); soluble in concentrated hydrochloric acid; dissolves in aqueous caustic soda. *Stannic chloride*, boiled with copper becomes stannous chloride. When *zinc* and *platinum* are placed in the solution, no black stain on the platinum; crystals of tin on the zinc.

Antimony.

Hydrogen sulphide, orange precipitate (Sb_2S_3), soluble in ammonium sulphide and in concentrated hydrochloric acid; insoluble in ammonium carbonate. *Water* in excess (with ammonium chloride if chlorides are absent), white precipitate (SbOCl), soluble in hydrochloric acid and in tartaric acid. *Zinc* and *platinum*, a black stain on the platinum (Sb), soluble in nitric acid and in ammonium sulphide.

Arsenic.

Hydrogen sulphide, yellow precipitate, soluble in ammonium sulphide and in ammonium carbonate; insoluble in concentrated hydrochloric acid. *Metallic copper*, boiled with the liquid after acidifying with hydrochloric acid, is covered with a shining grey deposit (As_2Cy_3), which, when heated in a tube, yields a sublimate of arsenious oxide (Reinsch's test) (Clark, Chem. Soc. Trans. 1893, 63, 884, 886). *Nascent hydrogen* produced from zinc and dilute sulphuric acid reduces arsenic compounds to volatile arsine (AsH_3), which decomposes on gently heating, giving an arsenic deposit soluble in aqueous hypochlorites. Antimony compounds under these conditions also give a black deposit (antimony), insoluble in hypochlorites (Marsh's test). Zinc and caustic soda reduce arsenic compounds, liberating arsine, which produces a yellow-to-brown stain on mercuric chloride paper (Gutzeit's test, Chem. Soc. Trans. 1901, 79, 715).

Arsenites. Ammonio-silver nitrate, yellow precipitate (Ag_3AsO_3), soluble in nitric acid and ammonia. *Ammonio-cupric sulphate*, bright-green precipitate ($CuHAsO_3$), turns red by boiling with caustic soda.

Arsenates. Ammonio-silver nitrate, brick-red precipitate (Ag_3AsO_4), soluble in nitric acid and ammonia. *Ammonium chloride, ammonia,* and *magnesium sulphate*, white crystalline precipitate (NH_4MgAsO_4). *Ammonio-cupric sulphate*, pale-blue precipitate, turned black by boiling with caustic soda.

When arsenic acid or arsenates are present, they should be reduced by heating with sulphurous acid or ammonium iodide or hydriodic acid (Bull. Soc. chim. Belg. 1909, 23, 88) before applying hydrogen sulphide or Reinsch's test (Usher and Travers, Chem. Soc. Trans. 1905, 87, 1370).

Platinum.

Hydrogen sulphide, brown precipitate (PtS_2) on heating, soluble in ammonium sulphide. *Ammonium chloride* or *potassium chloride*, yellow crystalline precipitate (M_2PtCl_6), less soluble in presence of alcohol. *Potassium iodide*, in dilute solution red colouration (K_2PtI_6), very delicate test. *Stannous chloride*, in dilute solution, brownish-red colouration, delicate test.

Palladium.

Hydrogen sulphide, black precipitate (PdS), insoluble in ammonium sulphide; soluble in hot hydrochloric acid and in aqua regia. *Potassium iodide*, black precipitate (PdI_2), somewhat soluble in excess. *Mercuric cyanide*, yellowish white, gelatinous precipitate ($PdCy_2$), readily soluble in ammonia. *Ammonium chloride*, no precipitate (diff. from Pt); on addition of chlorine water, orange precipitate ($(NH_4)_2PdCl_6$). *Potassium chloride*, precipitate ($2KCl{\cdot}PdCl_2$) only in very concentrated solutions.

α-Nitroso-β-naphthol dissolved in 50 p.c. acetic acid gives a voluminous red-brown precipitate in solutions containing only as little as 1 part palladium in 1,000,000.

Iridium.

Hydrogen sulphide, decolourisation followed by brown precipitate (Ir_2S_3), soluble in ammonium sulphide. *Caustic potash*, a greenish colouration which, on heating with exposure to air, changes slowly to azure blue (diff. from Pt). *Ammonium chloride* or *potassium chloride*, dark-brown or red precipitate (double chloride), insoluble in a saturated solution of the precipitant. Both salts become olive green with potassium nitrite and other reducing agents, especially in hot solutions. *Strong sulphuric acid* and *ammonium nitrate*, on heating, blue colouration.

Osmium.

Hydrogen sulphide, in acid but not in neutral solution, black precipitate (OsS_4), insoluble in ammonium sulphide. *Nitric acid* on boiling oxidises osmium compounds to osmic tetroxide (OsO_4), characteristic odour and yellow solution in caustic soda.

Ruthenium.

Hydrogen sulphide, blue solution followed by brown precipitate of ruthenium sulphide. *Sodium thiosulphate* in ammoniacal solution to dilute solutions of ruthenium, a purplish-red colouration. *Zinc* reduces $RuCl_3$, giving a blue solution and then precipitating ruthenium.

Rhodium.

Hydrogen sulphide, on warming, black precipitate (Rh_2S_3), insoluble in ammonium sulphide; soluble in boiling nitric acid. *Potassium nitrite*, warmed with sodium rhodium chloride, gives orange-yellow precipitate ($K_3Rh(NO_2)_6$)

Gold.

Hydrogen sulphide, black precipitate (Au_2S_3) in cold, brown precipitate (Au_2S) in hot, solution; soluble in yellow ammonium sulphide. *Oxalic acid* or *ferrous sulphate*, brown or purple precipitate, yellow and lustrous when rubbed. *Stannous* and *stannic chlorides*, purplish precipitate, insoluble in hydrochloric acid. *Hydrogen peroxide*, in very dilute alkaline solution, liberates finely divided gold having a beautiful blue shimmer.

A solution of colourless *m*-phenylenediamine (5 : 1000) gives an immediate violet colouration with a dilute solution of a gold salt.

Molybdenum.

Hydrogen sulphide, brownish-black precipitate (MoS_3) on heating, soluble in ammonium sulphide. *Sodium phosphate*, in presence of nitric acid, yellow precipitate on heating, soluble in ammonia and in excess of the alkaline phosphate. *Potassium thiocyanate* and zinc or stannous chloride, red colouration due to $Mo(CNS)_4$ soluble in ether. *Concentrated sulphuric acid*, when strongly heated with molybdenum compounds, develops a deep-blue colouration. *Phenylhydrazine*, in 50 p.c. acetic acid, red colouration (Ber. 1903, 36, 512).

Hydrogen peroxide, in presence of ammonia gives a cherry-red colouration.

Selenium.

Hydrogen sulphide, yellow precipitate, becoming dark on heating, soluble in ammonium sulphide. *Sulphurous acid*, in presence of hydrochloric acid, a red precipitate, which becomes grey on heating, and is soluble in potassium cyanide. *Stannous chloride* and other reducing agents behave in a similar manner. *Barium chloride*, (i.) white precipitate ($BaSeO_3$), soluble in dilute hydrochloric acid; (ii.) white precipitate ($BaSeO_4$), insoluble in dilute hydrochloric acid; soluble in the strong acid, evolving chlorine. *Concentrated sulphuric acid*, green colouration.

Tellurium.

Hydrogen sulphide, brown precipitate (TeS_2) at once from tellurites, but from tellurates only after boiling with hydrochloric acid. *Potassium iodide*, to tellurite in acid solution, black precipitate (TeI_4). *Reducing agents* ($SnCl_2$,Zn), black precipitate (Te). *Concentrated sulphuric acid*, carmine colouration.

Aluminium.

Ammonia, white gelatinous precipitate (AlH_3O_3), insoluble in excess and in ammonium carbonate; soluble in acids. *Caustic potash* or *soda*, white gelatinous precipitate (Al_3HO_3), soluble in excess; reprecipitated on adding ammonium chloride and heating.

Chromium.

Chromic salts. Ammonia, greenish or purplish precipitate (CrH_3O_3), soluble in acids; insoluble in ammonium carbonate. *Caustic potash* or *soda*, green precipitate (CrH_3O_3), soluble in excess, but reprecipitated on boiling.

Chromates. Hydrogen sulphide in acid solution, reduction to chromic salt with change of colour to green. *Lead acetate*, bright yellow precipitate ($PbCrO_4$), insoluble in acetic acid. *Silver nitrate*, dark-red precipitate (Ag_2CrO_4), soluble in nitric acid.

Iron.

Ferrous salts. Ammonium sulphide, black precipitate (FeS), soluble in acids. *Ammonia* or *caustic potash* or *soda*, white precipitate, rapidly becoming green and then brown. *Potassium ferrocyanide*, white precipitate, gradually becoming dark blue. *Potassium ferricyanide*, dark-blue precipitate ($Fe_3(FeCy_6)_2$). *Potassium thiocyanate*, no reaction.

Ferric salts. Ammonium sulphide, black precipitate ($2FeS + S$, or Fe_2S_3), soluble in acids. *Ammonia* or *caustic potash* or *soda*, reddish-brown precipitate (FeH_3O_3), soluble in acids. *Potassium ferrocyanide*, dark-blue precipitate ($Fe_4(FeCy_6)_3$), insoluble in dilute acids. *Potassium ferricyanide*, no precipitate; greenish-brown colouration. *Potassium thiocyanate*, blood-red colouration; not affected by boiling or by hydrochloric acid.

Thorium.

Ammonia, *caustic soda*, or *potash*, white gelatinous precipitate ($Th(OH)_4$), insoluble in excess. *Ammonium* or *sodium carbonate*, white precipitate, basic carbonate; soluble in excess. *Oxalic acid*, white precipitate ($Th(C_2O_4)_2,2H_2O$), insoluble in excess and insoluble in mineral acids, but soluble in ammonium oxalate. *Potassium fluoride* or *hydrofluoric acid*, white precipitate (ThF_4). *Potassium sulphate*, white crystalline precipitate ($2K_2SO_4,Th(SO_4)_2,2H_2O$).

Cerium.

Ammonia, white precipitate of basic salt, insoluble in excess. *Caustic potash* or *soda*, white precipitate ($Ce(OH)_3$), insoluble in excess; becomes yellow when exposed to air. *Oxalic acid*, white precipitate ($Ce_2(C_2O_4)_3$), insoluble in excess, but soluble in a large quantity of hydrochloric acid. *Potassium sulphate*, white precipitate even in somewhat acid solutions ($CeK_3(SO_4)_3$), insoluble in saturated solution of potassium sulphate. *Hydrogen peroxide*, in ammoniacal solution, orange-brown precipitate.

Glucinum.

Ammonia, white precipitate (GlH_2O_2), insoluble in excess. *Caustic potash* or *soda*, the same precipitate, soluble in excess, but reprecipitated on boiling (diff. from Al). *Ammonium carbonate*, white precipitate, easily soluble in excess (diff. from Al).

Glacial acetic acid dissolves $Gl(OH)_2$ or $GlCO_3$, and the residue, after evaporating to dryness, is the basic acetate ($Gl_4O(CH_3{\cdot}CO_2)_6$), readily soluble in chloroform, ether, acetone, the alcohols, and other organic media; dissolves unchanged in glacial acetic acid; it melts at 283°–284°, and can be sublimed without decomposition. *Sodium hydrogen carbonate*, 10 p.c. dissolves $Gl(OH)_2$; dilution to 1 p.c. causes reprecipitation.

Uranium.

Ammonia, *caustic potash*, or *soda*, yellow precipitate, insoluble in excess, but readily soluble in ammonium carbonate. *Ammonium sulphide*, brown precipitate, readily soluble in ammonium carbonate. *Potassium ferrocyanide*, chocolate-brown precipitate, readily decomposed by alkalis, yielding yellow alkali diuranates.

Titanium.

Ammonia, *caustic potash*, or *soda*, or *ammonium sulphide*, white precipitate (H_2TiO_3), insoluble in excess; soluble in dilute sulphuric and hydrochloric acids. *Potassium ferrocyanide*, dark-brown precipitate. *Sodium thiosulphate*, complete precipitation on boiling. *Hydrogen peroxide*, to a slightly acid solution of titanium sulphate; orange-red colouration; weakened by fluorides. A solution of thymol in acetic acid mixed with sulphuric acid gives a more intense colouration, also bleached by fluorides. *Reduc-*

ing agents ($SnCl_2$ or Zn and HCl) produce a violet colouration ($TiCl_3$).

Catechol added to dilute solutions of titanic or titanous salts, yellowish-orange colouration, very delicate test, but interfered with by mineral acids or alkalis (Ber. 1909, 42, 4341).

Zirconium.

Ammonia, ammonium sulphide, caustic soda, white gelatinous precipitate, dissolving in dilute acid, but less readily after boiling; precipitation prevented by tartaric acid. *Oxalic acid*, white precipitate ($Zr(C_2O_4)_2$), readily soluble in ammonium oxalate or in excess of oxalic acid. *Hydrogen peroxide*, white milky precipitate (Zr_2O_5), evolving chlorine when boiled with hydrochloric acid. *Turmeric paper*, moistened with acid solution of zirconium salt, becomes reddish-brown on drying.

Zinc.

Ammonium sulphide, white precipitate (ZnS), soluble in dilute hydrochloric acid; insoluble in acetic acid and in alkalis. *Caustic potash* or *soda*, white precipitate (ZnH_2O_2), soluble in excess. *Potassium ferrocyanide*, white precipitate, insoluble in dilute hydrochloric acid (Zn_2FeCy_6).

Manganese.

Ammonium sulphide, pink precipitate (MnS), soluble in dilute hydrochloric acid and in acetic acid. *Caustic potash* or *soda*, white precipitate (MnH_2O_2), insoluble in excess, becoming brown on exposure to air. Boiled with dilute *nitric acid* and *lead peroxide* (in absence of chlorine), a purplish crimson solution of permanganic acid.

Nickel.

Ammonium sulphide, black precipitate (NiS), somewhat soluble in excess; insoluble in cold dilute hydrochloric acid; soluble in strong acids. *Caustic potash* or *soda*, pale-green precipitate (NiH_2O_2), insoluble in excess. *Potassium cyanide*, precipitate ($NiCy_2$), soluble in excess, forming $NiCy_2,2KCy$, which is not altered when boiled with exposure to air. This solution, heated with excess of sodium hypochlorite solution, or mixed with bromine in the cold, yields a precipitate of black nickelic hydroxide (NiH_3O_3). *Dimethylglyoxime* ($CH_3·C(NOH)·C(NOH)·CH_3$) (Tschugaeff, Ber. 1905, 38, 2520), added to ammoniacal or acetic acid solution of nickel salts, scarlet precipitate (distinction from cobalt). *Dicyanodiamidine* (H. Grossmann and W. Heilborn, Ber. 1908, 41, 1878) added to ammoniacal solutions of cobalt and nickel salts containing excess of sucrose, yellow crystalline precipitate ($Ni(N_4H_5C_2O)_2,2H_2O$), the presence of cobalt indicated by the reddish-violet colour of the solution.

An alcoholic ammoniacal solution of α-benzildioxime gives an intense red precipitate $C_{28}H_{22}N_4O_4Ni$ (Tschugaeff, Zeitsch. anorg. Chem. 1905, 46, 144; Atack, Analyst, 1913, 316).

Cobalt.

Ammonium sulphide, black precipitate (CoS), insoluble in cold dilute hydrochloric acid; soluble in strong acids. *Caustic potash*, pale-blue precipitate (CoH_2O_2), slightly soluble in excess, forming a blue solution. *Potassium cyanide*, precipitate ($CoCy_2$), soluble in excess, forming $CoCy_2,4KCy$, and when this solution is boiled with exposure to air it is changed to K_3CoCy_6, which is not precipitated by sodium hypochloride or bromine. *Potassium nitrite* to dilute acetic acid solutions, yellow crystalline precipitate ($K_3Co(NO_2)_6$). *Nitroso-β-naphthol* $NO·C_{10}H_6·OH$ (Ilinski and Knorre, Ber. 18, 699) dissolved in dilute acetic acid added to feebly acid solutions of cobalt and nickel, brick-red precipitate ($Co(NO·C_{10}H_6·O)_3$); solution examined for nickel (Chaplin, J. Amer. Chem. Soc. 1907, 29, 1029).

Vanadium.

Ammonium sulphide, dark-brown solution, which when acidified yields a brown precipitate (V_2S_4). *Ammonium chloride*, white precipitate of ammonium meta-vanadate (NH_4VO_3). *Potassium ferrocyanide*, in acid solution, a green precipitate. If a solution of an alkaline vanadate is agitated with *hydrogen peroxide* and *ether*, the solution acquires a deep purplish-red colour, but the ether remains colourless. *Mild reducing agents* (SO_2, H_2S, HBr, alcohol, &c.) reduce vanadates in acid solutions to blue divanadyl salts. *Strong reducing agents* (zinc and aluminium with acids) produce a series of colour changes—blue, green, and violet.

Columbium.

Hydrogen fluoride and *potassium fluoride* produce potassium columbo-fluoride, which when boiled in aqueous solution yields potassium columbium oxyfluoride (K_2CbOF_5,H_2O) (solubility 1 in 12·5 cold water). *Mineral acids*, partial precipitation of columbic acid from alkali columbates: *zinc* and *acid*, blue colouration, turning brown; *potassium ferrocyanide*, greyish-green precipitate.

Tantalum.

Hydrogen fluoride and *potassium fluoride* produce potassium tantalofluoride (K_2TaF_7) (solubility 1 in 154 cold water), separating in colourless needles. *Mineral acids*, white precipitate of tantalic acid. *Potassium ferrocyanide*, reddish-brown precipitate (*v.* Weiss and Landecker, Zeitsch. anorg. Chem. 1909, 64, 65).

Calcium.

Ammonium carbonate, white precipitate ($CaCO_3$), soluble in acids. *Sulphuric acid*, white precipitate only in very concentrated solutions. *Ammonium oxalate*, white precipitate (CaC_2O_4), insoluble in acetic and oxalic acids, but soluble in hydrochloric acid.

Strontium.

Ammonium carbonate, white precipitate, soluble in acids ($SrCO_3$). *Ammonium sulphate*, white precipitate, especially on boiling. *Ammonium oxalate*, white precipitate (SrC_2O_4), soluble in hydrochloric acid; insoluble in acetic acid. *Sulphuric acid* or *calcium sulphate*, white precipitate ($SrSO_4$), forming slowly.

Barium.

Ammonium carbonate, white precipitate ($BaCO_3$), soluble in acids. *Ammonium oxalate*, white precipitate (BaC_2O_4), soluble in hydrochloric acid; insoluble in acetic acid. *Sulphuric acid* or *calcium sulphate*, an immediate white precipitate, insoluble in acids and alkalis. *Potassium chromate*, yellow precipitate ($BaCrO_4$), insoluble in acetic acid.

Magnesium.

Sodium phosphate, in presence of ammonia and ammonium chloride, white precipitate, rapidly becoming crystalline ($NH_4MgPO_4 6H_2O$). Forms slowly in dilute solutions, formation being accelerated by agitation and by rubbing the sides of the beaker with a glass rod; soluble in acids.

Potassium.

Chloroplatinic acid H_2PtCl_6, yellow crystalline precipitate (K_2PtCl_6), somewhat soluble in water, insoluble in alcohol. *Sodium hydrogen tartrate*, in neutral or feebly acid solutions, a white crystalline precipitate ($KHC_4H_4O_6$), forming slowly in dilute solutions. If the solution contains free mineral acids, nearly neutralise with soda and add sodium acetate (*cf.* Winkler, Zeitsch. angew. Chem. 1913, 26, 208; Analyst, 1913, 295).

Sodium cobaltinitrite in acetic acid solution, yellow precipitate ($K_2NaCo(NO_2)_6$). *Sodium 1-amino-β-naphthol-6-sulphonate* (eikonogen) in 5–10 p.c. solutions, crystalline precipitate ($KSO_3{\cdot}C_{10}H_5(NH_2){\cdot}OH$); negative results with ammonium and magnesium salts (Alvarez, Chem. Soc. Abstr. 1905, ii. 355).

Ammonium.

Ammonium salts are readily volatile. *Heated with lime, caustic potash,* or *soda,* ammonia gas is given off, and is recognised by its smell and its action on test paper.

Chloroplatinic acid, yellow crystalline precipitate ($(NH_4)_2PtCl_6$), slightly soluble in water: insoluble in alcohol. *Sodium hydrogen tartrate*, white crystalline precipitate ($NH_4HC_4H_4O_6$), forming slowly in dilute solutions.

Nessler's reagent (K_2HgI_4 and KOH), brownish-red precipitate or colouration (NHg_2I,H_2O), very delicate test. Equally delicate is the blue colouration which is developed when an ammonium compound is treated with a solution of phenol and a hypochlorite (eau de Javel).

Sodium.

Flame colouration, intense yellow.

Although all sodium salts are more or less soluble, some dissolve only sparingly, *e.g.* sodium oxalate and sodium *a*-naphthylamine-8-sulphonate.

Potassium pyroantimonate, white crystalline precipitate ($Na_2H_2Sb_2O_7{\cdot}6H_2O$) (J. Amer. Chem. Soc. 1909, 31, 634); from neutral or slightly alkaline solutions.

Dihydroxytartaric acid, colourless precipitate ($CO_2Na{\cdot}C(OH)_2{\cdot}C(OH)_2\,CO_2Na$) (Fenton, Chem. Soc. Trans. 1895, 67, 48). *Solution of bismuth nitrate in 50 p.c. potassium nitrite containing cæsium nitrite*, yellow crystalline precipitate ($5Bi(NO_2)_3,9CsNO_2,6NaNO_2$); very delicate test, not interfered with by lithium and metals of alkaline earths (Ball, Chem. Soc. Trans. 1909, 95, 2126). Sodium chloride, obtained by slow evaporation of a solution acidified with hydrochloric acid, crystallises in distinct cubes.

Lithium.

Chloroplatinic acid, no precipitate.

Sodium phosphate, in alkaline solution; white precipitate (Li_3PO_4), soluble in hydrochloric acid, not reprecipitated by ammonia except on boiling. Lithium chloride is soluble in ethyl or amyl alcohol, and in pyridine. *Ammonium hydrogen fluoride*, white precipitate (LiF).

Cæsium.

Flame colouration, violet.

Chloroplatinic acid, yellow crystalline precipitate (Cs_2PtCl_6), insoluble in boiling water, *Tartaric acid*, crystalline precipitate, somewhat soluble in water. *Stannic chloride*, white precipitate (Cs_2SnCl_6). *Lead chloride dissolved in chlorine water*, yellow precipitate (Cs_2PbCl_6). Cæsium carbonate is soluble in alcohol (diff. from K, Rb).

Rubidium.

Flame colouration, violet.

Chloroplatinic acid, yellow crystalline precipitate (Rb_2PtCl_6), insoluble in boiling water. *Tartaric acid*, white crystalline precipitate, less soluble than the cæsium compound (Reactions of Cs and Rb, *v.* Wells, Amer. J. Sci. [3] 43, 17 and 46, 186, and 265).

ACID RADICALS.

The acid radicals are arranged partly in the order of the systematic separation and partly with a view to bring together those acids which are commonly associated or which resemble one another in their reactions. In all cases, unless otherwise specified, it is important that the solution should be neutral.

Sulphates.

Barium chloride, white precipitate ($BaSO_4$), insoluble in acids and alkalis.

Sulphites.

Hydrochloric acid, sulphur dioxide evolved, but no sulphur precipitated. *Barium chloride*, white precipitate ($BaSO_3$), soluble in hydrochloric acid. *Iodine solution*, sulphites are converted into sulphates. Neutralise, then *slightly* acidify with acetic acid; add excess of *zinc sulphate*, a small quantity of *sodium nitroprusside* and *potassium ferrocyanide*. The precipitate of zinc ferrocyanide has a pink colour.

Strontium chloride, white precipitate ($SrSO_3$), different from thiosulphate SrS_2O_3, being much more soluble.

Hyposulphites ('hydrosulphites,' *e.g.* $Na_2S_2O_4$, $2H_2O$) owe their technical application to their reducing action on indigotin and its sulphonic acids—the colour is discharged (indigo-white). *Silver nitrate*, black precipitate (Ag). *Mercuric chloride*, black precipitate (Hg). *Copper sulphate*, reddish precipitate (Cu and Cu_2H_2), in very dilute solution, colloidal copper.

Thiosulphates.

Hydrochloric acid, sulphur dioxide evolved and sulphur precipitated. *Silver nitrate*, white precipitate ($Ag_2S_2O_3$), rapidly changing to black (Ag_2S), soluble in excess of alkaline thiosulphate, forming a much more stable solution. With *sodium nitroprusside, zinc sulphate,* and *potassium ferrocyanide*, the precipitate is white. *Iodine solution* converts soluble thiosulphates into tetrathionates, which give no precipitate with barium chloride. *Ferric chloride*, transient violet colouration ($Fe_2(S_2O_3)_3$).

Persulphates (*e.g.* $K_2S_2O_8$).

The dry salts evolve oxygen on heating. *Barium chloride*, no precipitate in the cold, on warming oxygen evolved and $BaSO_4$ precipitated. *Silver nitrate*, black precipitate (silver peroxide). *Other metallic salts* (Pb, Mn, Co, and Ni) yield their hydrated peroxides.

Monopersulphuric acid (*Caro's acid*) $HO{\cdot}SO_2{\cdot}O{\cdot}OH$, produced by adding a persulphate to cold concentrated sulphuric acid, and pouring the mixture on to ice. *Aromatic amines* (*e.g.* $p\text{-}Cl{\cdot}C_6H_4{\cdot}NH_2$) give coloured oxidation products with persulphates and nitroso- compounds (*e.g.* $Cl{\cdot}C_6H_4{\cdot}NO$) with Caro's acid.

Thionic acids (*v.* Chem. Soc. Trans. 1880, 608).

Sulphides.

Hydrochloric acid, in most cases evolution of hydrogen sulphide, especially on heating. *Lead nitrate* or *acetate,* black precipitate (PbS). *Silver nitrate,* black precipitate (Ag_2S), insoluble in ammonia, sodium thiosulphate, and potassium cyanide. *Sodium nitroprusside,* in alkaline solutions an intense but somewhat fugitive violet colouration.

Phosphates.

Barium chloride, white precipitate $Ba_3(PO_4)_2$, soluble in dilute acids. *Calcium chloride,* white precipitate ($Ca_3(PO_4)_2$), soluble in acetic acid. *Silver nitrate,* yellow precipitate (Ag_3PO_4), soluble in nitric acid and in ammonia. *Pyrophosphates* and *metaphosphates* give white precipitates of their silver salts with silver nitrate, but metaphosphates alone, unlike ortho- and pyro-phosphates, coagulate albumin. *Magnesium sulphate,* in presence of ammonium chloride and ammonia, white crystalline precipitate ($NH_4MgPO_4 6H_2O$), soluble in acids. *Ammonium molybdate,* in nitric acid solution, on heating, a yellow precipitate ($((NH_4)_3PO_4 \cdot 12MoO_3)$) soluble in ammonia, and soluble in excess of an alkaline phosphate.

Phosphites.

Barium chloride, white precipitate ($BaHPO_3$), soluble in hydrochloric acid. *Silver nitrate,* precipitate of metallic silver, especially in presence of ammonia, and on heating. *Mercuric chloride,* white precipitate (Hg_2Cl_2), becoming grey (Hg). Heated with *nitric acid,* phosphites are converted into phosphates. Heated alone, phosphites evolve phosphine. *Copper sulphate,* pale blue precipitate.

Hypophosphites.

Heated alone, evolve phosphine. *Barium chloride,* white precipitate only in strong solution ($Ba(H_2PO_2)_2$). *Silver nitrate,* metallic silver precipitated. *Copper sulphate,* brown precipitate, cuprous hydride (Cu_2H_2).

Carbonates.

Hydrochloric acid, effervescence, with evolution of carbonic anhydride, which turns lime water turbid. *Barium chloride,* white precipitate ($BaCO_3$), soluble in acids with effervescence. *Mercuric chloride,* red precipitate (basic carbonate); bicarbonates give only a yellowish opalescence. *Calcium sulphate,* white precipitate, immediately with carbonate, but only after standing with bicarbonate (Leys, J. Pharm. Chim. 1897, (vi.) 6, 441).

Borates.

Barium chloride, white precipitate in not too dilute solutions, soluble in acids. *Silver nitrate,* in strong solution, white precipitate ($AgBO_2$) in dilute solution, dark-grey deposit (Ag_2O).

Mix the solid substance with concentrated sulphuric acid in a small crucible, add alcohol, and ignite; the alcohol flame is green, especially at the edges. Mix the solid substance with three parts potassium hydrogen sulphate and one part powdered fluorspar, and heat on platinum wire in the cold area of the flame; a bright-green colouration (due to BF_3) is observed. *Turmeric paper,* moistened with acid solution of boric acid, becomes reddish brown on drying.

Silicates.

Solutions of silicates heated with acids, ammonium chloride, or ammonium carbonate, deposit silicic acid. Dilute solutions must be evaporated to dryness, and on treating the residue with dilute hydrochloric acid insoluble silica is left.

Most silicates are insoluble in water; some are decomposed by acids; others are only decomposed by fusion with about four times their weight of a mixture of equal parts of sodium and potassium carbonates.

Silicofluorides.

Concentrated sulphuric acid, in leaden or platinum capsule, hydrogen fluoride and silicon fluoride are evolved. *Barium chloride,* colourless crystalline precipitate $BaSiF_6$. Silicofluorides on heating evolve silicon fluoride, leaving residues of metallic fluorides.

Thorium nitrate precipitates hydrofluosilicic acid quantitatively from soluble hydrofluosilicates.

Oxalates.

Barium chloride or *calcium chloride,* white precipitate, insoluble in acetic acid, but soluble in hydrochloric acid.

Acidify with sulphuric acid, and add potassium permanganate; the colour of the latter is rapidly and completely discharged.

Heat the solid substance with concentrated sulphuric acid; carbonic anhydride and carbonic oxide are evolved. The latter burns with a blue flame.

Fluorides.

Barium chloride, white precipitate (BaF_2), soluble in hydrochloric acid. *Silver nitrate,* no precipitate with soluble fluorides. *Concentrated sulphuric acid,* especially when heated, produces hydrogen fluoride, which attacks glass. The substance and acid are placed in a small leaden or platinum crucible, which is covered with a watch-glass protected by a thin coating of wax, part of which has been scratched away so as to expose the glass.

Thorium nitrate added to a solution of an alkali fluoride acidified with acetic or nitric acid gives a gelatinous precipitate of thorium fluoride ThF_4.

Chlorides.

Silver nitrate, a white precipitate (AgCl), insoluble in nitric acid, soluble in ammonia; darkens when exposed to light. *Manganese dioxide* and *sulphuric acid,* evolution of chlorine on heating. *Potassium dichromate* and *strong sulphuric acid,* evolution of chromyl chloride on heating. This forms with ammonia a yellow solution of ammonium chromate.

Bromides.

Silver nitrate, yellowish-white precipitate (AgBr), insoluble in nitric acid; moderately soluble in ammonia; readily soluble in potassium cyanide or sodium thiosulphate. *Manganese dioxide* and *sulphuric acid,* orange vapours of bromine, which turn starch paste orange. *Chlorine water* liberates bromine, which dissolves in ether or carbon disulphide, forming an orange-brown solution. Bromides heated with *potassium dichromate* and *strong sulphuric acid* yield bromine, which forms a colourless solution with ammonia.

Iodides.

Silver nitrate, yellow precipitate (AgI), insoluble in nitric acid or ammonia; soluble in potassium cyanide or sodium thiosulphate. *Manganese dioxide* and *sulphuric acid* yield violet vapours of iodine, which colour starch paste blue. *Chlorine water, bromine water*, or *potassium dichromate in presence of hydrochloric acid*, liberates iodine, which turns starch paste an intense blue. The colour disappears on heating, and reappears on cooling. The liberated iodine may be agitated with carbon disulphide or chloroform, when it yields a violet solution. *Nitrogen oxides in sulphuric acid* likewise liberate iodine, but do not liberate bromine unless added in large excess.

Cyanides.

Silver nitrate, white precipitate (AgCN), insoluble in nitric acid, but soluble in ammonia, sodium thiosulphate, or excess of the alkaline cyanide.

Add ferric chloride and ferrous sulphate; make alkaline with caustic potash or soda, and then acidify with hydrochloric acid. A dark blue precipitate of Prussian blue is formed.

Evaporate the solution with an excess of yellow ammonium sulphide to complete dryness on a water-bath; dissolve in very dilute hydrochloric acid, and add ferric chloride; a blood-red colouration is produced.

Most cyanides evolve hydrocyanic acid, recognisable by the smell, when treated with hydrochloric or sulphuric acid.

Mercuric cyanide cannot be recognised by these tests. It yields cyanogen when heated in a closed tube, and is decomposed when heated with strong sulphuric acid.

Ferrocyanides.

Silver nitrate, white precipitate (Ag_4FeCy_6), insoluble in nitric acid and sparingly soluble in ammonia; soluble in potassium cyanide. *Ferric chloride*, dark-blue precipitate ($Fe_4(FeCy_6)_3$). *Ferrous sulphate*, white precipitate, rapidly becoming blue. *Copper sulphate*, chocolate-brown precipitate (Cu_2FeCy_6), or in very dilute solution a brown colouration.

Ferricyanides.

Silver nitrate, orange precipitate (Ag_3FeCy_6), soluble in ammonia; insoluble in nitric acid. *Ferrous sulphate*, dark-blue precipitate ($Fe_3(FeCy_6)_2$), insoluble in dilute acids; decomposed by alkalis. *Ferric chloride*, a greenish-brown colouration.

Thiocyanates.

Silver nitrate, white precipitate (AgCNS), soluble in ammonia; insoluble in nitric acid. *Ferric chloride*, blood-red colouration, not affected by boiling nor by hydrochloric acid; decolourised by mercuric chloride. *Copper sulphate*, a black precipitate changing to white ($Cu_2(CNS)_2$) on standing or addition of a reducing agent. *Moderately strong sulphuric acid* evolves carbon oxysulphide, which burns to carbon dioxide and sulphur dioxide. *Cobalt chloride* and the solution shaken up with ether and amyl alcohol, azure-blue colouration ($K_2Co(CNS)_4$).

Cyanates.

Cobalt chloride, in aqueous alcoholic solution, blue soluble double salt ($K_2Co(CNO)_4$), decomposed by excess of water.

Nitrates.

Sulphuric acid evolves nitric acid on heating; if metallic copper is added, red-brown nitrogen oxides are given off.

The neutral solution is mixed with ferrous sulphate, and concentrated sulphuric acid is poured down the side of the tube so as to form a layer at the bottom; a dark-brown ring is formed at the junction of the two liquids. Iodine and bromine must be removed before applying this test, and the liquid must be cold. Nitrate in presence of nitrite: destroy nitrite by boiling acetic acid solution with urea or hydrazine sulphate; then add potassium iodide, starch, and a fragment of zinc; then colouration denotes nitrate.

Nitrites.

Silver nitrate, a white precipitate in concentrated solutions.

Mix the solution with potassium iodide and starch and acidify with acetic acid; a deep-blue colouration is produced, owing to the liberation of iodine. Nitrites heated with dilute acids evolve nitrogen oxides. *Metaphenylenediamine hydrochloride*, Bismarck brown colouration.

A dilute solution of *a-naphthylamine* and *sulphanilic acid* acidified with acetic acid; a red colouration of azo- compound (*cf.* Zeitsch. angew. Chem. 1900, 235).

Dimethylaniline hydrochloride, added to an acidulated solution containing nitrous acid, gives a yellow colour depending on the formation of paranitrosodimethylaniline (Miller, Analyst, 1912, 37, 345).

Hypochlorites.

Silver nitrate, a white precipitate of silver chloride. *Lead nitrate*, a white precipitate becoming orange-red, finally brown. *Manganous salts*, a brown precipitate (MnO_2,xH_2O). *Indigo solution*, decolourised even in an alkaline solution.

Chlorates.

Warm a small quantity of the solid with concentrated sulphuric acid; a yellow explosive gas is produced with detonations.

Acidify the solution with sulphuric acid, add indigo solution, and then sulphurous acid or a sulphite drop by drop; the colour of the indigo is discharged.

Perchlorates.

Concentrated sulphuric acid, no explosive gas. *Titanous sulphate*, perchlorates reduced to chlorides.

Bromates.

Silver nitrate, white precipitate, $AgBrO_3$, decomposed by hot hydrochloric acid with evolution of bromine. *Barium chloride*, white precipitate $Ba(BrO_3)_2$. *Sulphurous acid*, bromine liberated.

Iodates.

Silver nitrate, white curdy precipitate ($AgIO_3$), soluble in ammonia; reduced to yellow silver iodide by sulphurous acid. *Barium chloride*, white precipitate ($Ba(IO_3)_2$). *Sulphurous acid*, iodine liberated.

Periodates.

Silver nitrate, yellowish-white, red, or brown precipitate depending on the acidity of the periodate solution. *Barium chloride*, white precipitate. *Manganous sulphate*, red precipitate Mn_2HIO_6, turning brown. *Reducing agents* (H_2SO_3, $Ti_2(SO_4)_3$, Zn, etc.) convert periodates readily into iodides. *Mercuric nitrate*, orange-red precipitate $5HgO,I_2O_7$, different from iodates, which give white $Hg(IO_3)_2$.

Tartrates.

Calcium chloride, in excess, a white precipitate ($CaC_4H_4O_6$), soluble in acids and in potash solution. Complete precipitation requires time, and is promoted by vigorous agitation. *Potassium acetate*, in presence of free acetic acid, a white crystalline precipitate ($KHC_4H_4O_6$), forming slowly in dilute solutions. *Silver nitrate*, a white precipitate, soluble in nitric acid or ammonia. If the washed precipitate is dissolved in the least possible quantity of dilute ammonia, and the solution heated, the test-tube is coated with a mirror of metallic silver. *Ferrous sulphate*, followed by few drops of hydrogen peroxide and excess of caustic soda, bluish-violet colouration.

Citrates.

Calcium chloride, or *lime-water*, in excess in neutral solution, a white precipitate,

$$(Ca_3(C_6H_5O_7)_2)$$

only on boiling. *Potassium salts*, no precipitate. *Cadmium chloride*, gelatinous white precipitate $(Cd(C_6H_5O_7)_2)$, insoluble in hot water; soluble in acetic acid (diff. from tartrates). *Mercuric sulphate* (5 p.c.), following by potassium permanganate, white turbidity, mercuric acetonedicarboxylate (halogens should be absent) (Denigès).

Malates.

Calcium chloride, no precipitate even on boiling, except in strong solutions; precipitate in dilute solutions on adding alcohol. *Lime water*, no precipitate even on boiling. *Silver nitrate*, white precipitate $(Ag_2C_4H_4O_5)$, which becomes grey on boiling. *Lead acetate*, white precipitate $(PbC_4H_4O_5)$, which when washed melts in boiling water.

Succinates.

Barium chloride, or *calcium chloride*, no precipitate except after addition of alcohol. *Ferric chloride*, reddish-brown precipitate $(Fe_2(C_4H_4O_4)_3)$, soluble in acids; decomposed by ammonia.

Benzoates.

Hydrochloric acid, white crystalline precipitate of benzoic acid, slightly soluble in water. *Ferric chloride*, a buff precipitate $(Fe_2(C_4H_7O_5)_6)$, soluble in hydrochloric acid with liberation of benzoic acid; decomposed by ammonia. *Concentrated sulphuric* acid and *alcohol* on heating produce ethyl benzoate, distinctive odour. *Soda lime*: benzoates heated with this reagent are decomposed, evolving benzene.

Salicylates.

Ferric chloride, intense purple colour; not affected by glycerol; interfered with by alkalis, dilute mineral acids, tartaric, citric, and oxalic acids, and certain other substances such as borax, sodium phosphate, ammonium and sodium acetates. *Silver nitrate*, white precipitate in neutral solutions. *Bromine water*, white precipitate, which with sodium amalgam yields phenol. *Concentrated sulphuric acid* and *methyl alcohol* on heating give methyl salicylate ('oil of winter-green'). *Diazotised aniline* or *sulphanilic acid* gives an orange azo- compound.

Acetates.

Ferric chloride, a dark-red colouration, discharged on boiling, with precipitation of a basic ferric acetate. Also discharged by hydrochloric acid. Heated with *strong sulphuric acid*, acetic acid is evolved. If alcohol is added, ethyl acetate is formed and is recognised by the smell.

Formates.

Silver nitrate, a white precipitate in concentrated solutions; the solution or precipitate rapidly becomes black (Ag), especially on heating. *Ferric chloride*, a red colour, discharged on boiling, with precipitation of basic ferric formate; also discharged by hydrochloric acid.

A solid formate mixed with concentrated sulphuric acid gives off carbonic oxide even in the cold, but no carbonic anhydride.

Gallic acid.

Ferric chloride, in neutral solutions, a bluish-black precipitate or colouration. *Gelatin* or *albumin*, no precipitate. *Potassium cyanide*, red colouration, which disappears on standing, but reappears on agitation in presence of air. *Caustic soda*, green colouration gradually darkening, and with excess becoming brownish-red. *Lime water*, bluish-grey precipitate.

Tannic acid.

Ferric chloride, bluish-green or bluish-black precipitate or colouration. *Gelatin* or *albumin*, yellowish-white precipitate. *Potassium cyanide*, no colouration. *Caustic soda*, reddish-brown colouration gradually darkening. *Lime water*, grey precipitate.

Phenol.

Ferric chloride, violet colouration, destroyed by acids. *Bromine water*, white precipitate (tribromophenol and tribromophenol bromide). *Concentrated sulphuric acid* and a fragment of *sodium nitrite*, on gently warming, greenish blue solution, turned red when poured into water, and changed again to blue by caustic alkali.

Pyrogallol.

Silver nitrate or *Fehling's solution*, readily reduced. *Caustic alkalis*, brown solutions, rapidly darkening owing to absorption of oxygen. *Formaldehyde* and *strong hydrochloric acid*, white precipitate becoming red, and finally purple.

Uric acid.

Alkali urates reduce *silver nitrate*, and when heated with solid caustic soda, ammonia is evolved, and an alkali cyanide is produced. *Nitric acid*: evaporate solution to dryness on water-bath, reddish colouration, rendered violet by ammonia, and turned blue by caustic soda (Murexide test).

Quantitative Analysis.

GRAVIMETRIC METHODS.

A few metals are separated and weighed in the metallic condition, but the majority of metallic and acidic radicals are weighed in the form of one or other of their compounds. In order that a compound may be available for the determination of one of its constituents, it should be of perfectly definite composition and not highly hygroscopic or otherwise liable to alter; it must be insoluble in the liquid in which it is formed, and insoluble in an excess of the reagent; it must be easily freed from impurities, and capable of being brought into the proper condition for weighing without tedious and complicated operations. It is also desirable that the compound should contain only a small proportion of the constituent to be estimated, since the effect of the unavoidable error of experiment is thus minimised. An estimation of chlorine in the form of silver chloride is more accurate than an estimation of silver in the same way, since only one-fourth of the error of experiment represents chlorine, whilst three-fourths represent silver.

A description will first be given of a few typical gravimetric methods; then an alphabetical list of metals and acid radicals, with a summary of methods available in each case;

followed by a series of methods of separation of general applicability. Special methods for the analysis of technical products will be found in the articles dealing with these materials.

GENERAL METHODS OF ESTIMATION.

I *As Sulphides.*

(*a*) *With previous precipitation by hydrogen sulphide.* The solution should be moderately dilute and distinctly acidified with HCl, but any large quantity of this acid must be avoided. Nitric acid and nitrates, which should be absent as far as possible, may be removed by repeated evaporation with strong hydrochloric acid, but this treatment is not admissible if the metals present form volatile chlorides; if present, a much higher degree of dilution is necessary. In most cases precipitation is accelerated and the precipitate rendered more granular by keeping the liquid warm. A current of washed hydrogen sulphide is passed through the solution until it is thoroughly saturated, and the flask is closed and left in a warm place until the precipitate has settled. Molybdenum and the metals of the platinum group are only completely precipitated after prolonged treatment with the gas. The precipitate is protected from air as far as possible during filtration, and the liquid used for washing should contain hydrogen sulphide in order to prevent oxidation.

When arsenic is present, the liquid should be heated with pure sulphurous acid to reduce arsenic acid, and the excess of sulphurous acid expelled before treatment with hydrogen sulphide. In presence of antimony, tartaric acid should be added to prevent co-precipitation of basic antimony chloride.

When copper is precipitated as sulphide in presence of zinc, the copper sulphide should be washed once or twice with dilute hydrochloric acid of sp.gr. 1·05 containing hydrogen sulphide, and then with water also containing the gas.

(*β*) *With previous precipitation by ammonium sulphide.* Add to the warm solution a considerable quantity of ammonium chloride, which is found to promote precipitation and render the precipitate more granular, then ammonia to alkaline reaction, and a slight excess of ammonium sulphide. Close the flask and allow to stand in a warm place until the precipitate has settled. Protect from air as far as possible during filtration, and wash with water containing ammonium chloride and a little ammonium sulphide or hydrogen sulphide.

The precipitated sulphide is treated in one of two ways: it is collected on a weighed filter, dried at a definite temperature and weighed; or heated with sulphur in a current of hydrogen, and then weighed.

In the first case it is essential to ensure the absence of co-precipitated sulphur, and for this purpose the dried precipitate is treated with pure carbon disulphide and again dried, or, in the case of cadmium, mercury, or bismuth, the moist precipitate is treated with a warm concentrated solution of sodium sulphite, again washed, and dried.

When the sulphide is stable at a moderately high temperature and is not reduced by hydrogen, Rose's method is employed. The dry precipitate is separated from the filter, which is then burnt, and the precipitate and filter ash are introduced into a porcelain crucible and mixed with pure finely powdered sulphur. The crucible is provided with a perforated lid, through which passes a porcelain tube connected with a hydrogen apparatus. A current of purified and dried hydrogen is passed into the crucible, which is gradually heated to full redness until excess of sulphur is expelled, allowed to cool in a current of hydrogen, and weighed

Non-volatile sulphides may be collected in a wide Soxhlet tube and dried *in situ* over a ring burner at 300°, while a current of pure dry carbon dioxide is conducted through the tube. This treatment removes both moisture and co-precipitated sulphur (Cahen and Morgan, Analyst, 1909, 34, 3).

II. *As Oxide.*

(*a*) *With previous precipitation as hydroxide.* The solution is mixed with ammonium chloride, heated to boiling, and ammonia added in slight excess. A large excess of ammonia will partially redissolve some of the precipitate, and must be expelled by boiling. The precipitate is washed with hot water.

If ammonia is inadmissible, pure caustic potash or soda is used as the precipitant. Excess of alkali must be avoided, and the precipitate must be very thoroughly washed, since small quantities of alkali are somewhat firmly retained.

In both cases it is better to precipitate in a porcelain or platinum vessel than in glass.

Non-volatile carbon compounds, such as sugar, glycerol, alkaline, tartrates, and citrates, &c., more or less completely prevent precipitation of hydroxides by ammonia or caustic potash, or soda, and hence must first be removed by calcination. Moderately strong nitric acid attacks filter paper, forming soluble products, which prevent the precipitation of metallic hydroxides.

(*β*) *With previous precipitation as carbonate.* The solution is nearly neutralised, heated to boiling, and mixed with a slight excess of sodium carbonate, boiling being continued until all carbon dioxide is expelled. The precipitate is washed with hot water. Ammonium carbonate can be used in some cases, and has the advantage of not introducing a fixed alkali. In these cases the precipitate should be washed with water containing a little ammonia and ammonium carbonate.

The precipitated hydroxide or carbonate is placed in a crucible (with previous separation from the filter paper if the metal is easily reducible), and is gradually heated to full redness, care being taken that no reducing gases from the flame enter the crucible. Oxides of reducible metals must be heated in a porcelain crucible, but in other cases a platinum crucible may be used with advantage. If carbonates (or oxalates) are being converted into oxides, it is important to secure a circulation of air in order to remove carbon monoxide and carbon dioxide as fast as they are given off, and thus accelerate decomposition. This is done by inclining the crucible and placing the lid across the mouth in a slanting position.

III. *As reduced Metals.*

(*a*) In some cases the metal is precipitated as oxide, which is then dried and heated in hydrogen as in Rose's method for sulphides, the reduced metal being cooled in hydrogen and weighed. This method is especially valuable when, as in the case of cobalt, the oxide obstinately retains small quantities of alkali, which, however, can readily be removed from the reduced metal by washing with water.

(β) The other method is to mix the oxide, carbonate, &c., with five or six times its weight of ordinary potassium cyanide, and heat in a capacious porcelain crucible, at first cautiously and afterwards to complete fusion. When reduction is complete, the crucible is allowed to cool, and is tapped occasionally to promote the collection of the reduced metal in a single button. The cyanide is removed by treatment with water, the metal washed, dried, and weighed. Care should be taken that the metallic button does not contain small fragments of porcelain resulting from the corrosion of the crucible.

IV. *As Sulphate.*

Barium, strontium, and lead are precipitated from solutions in the ordinary way, but other metals are converted into sulphate by treatment with the strong acid, the method being only available when a single metal is present in combination with a volatile acid. The highly concentrated solution, or better, the solid substance, is mixed cautiously with concentrated sulphuric acid in a platinum crucible and then gently heated to expel excess of acid, the crucible being inclined and the lid placed in a slanting position across its mouth. A large excess of acid should be avoided, and care must be taken that the temperature is sufficient to expel the excess of free acid but not sufficient to decompose the sulphate. Sulphates of the alkalis and alkaline earths may be heated to redness. Bismuth sulphate and zinc sulphate decompose if heated above 400°; magnesium sulphate is not decomposed at 450°, nor barium or lead sulphate at 500° (G. H. Bailey). A temperature of about 350° is required to expel the last traces of free sulphuric acid. With lead or bismuth sulphate a porcelain vessel must be used.

GRAVIMETRIC DETERMINATION OF METALS AND ACID RADICALS.

Details of operations will be found under *General Methods of Estimation*, and electrolytic and volumetric methods will be indicated under appropriate headings.

Aluminium.

(*a*) As *oxide*, with previous precipitation with ammonium sulphide, ammonium carbonate, or as basic acetate (*v. Methods of separation*). The aluminium hydroxide is maintained in its insoluble hydrogel form by washing with dilute aqueous ammonium nitrate. The hydroxide may also be precipitated in a form suitable for filtration by boiling the solution of the aluminium salt with potassium iodide and potassium iodate (Stock, Ber. 1900, 33, 548; Compt. rend. 1900, 130, 175); or with bromine water (Jakob, Zeitsch. anal. Chem. 1913, 52, 651), when the precipitate is compact and not gelatinous.

(*b*) As *phosphate*. The solution is nearly neutralised, mixed with sodium acetate and a small quantity of acetic acid, heated to boiling, sodium phosphate added in excess, and the precipitate washed with hot water, heated, and weighed as aluminium phosphate ($AlPO_4$).

Ammonium.

(*a*) As *platinichloride* $(NH_4)_2PtCl_6$ (*v. Potassium*). The platinic chloride solution should be added before the liquid is heated, and evaporation should not quite be carried to complete dryness.

(*b*) By distillation (*v.* ACIDIMETRY).

Antimony.

(*a*) As *sulphide* Sb_2S_3. The precipitate is collected (i.) in a weighed Soxhlet tube on an asbestos mat, and dried at 280°–300° in a current of carbon dioxide (Analyst, 1909, 34, 3); or (ii.) in a Gooch crucible and dried in an air-oven in an atmosphere of carbon dioxide. An aliquot part is then placed in a porcelain boat, and heated in a glass tube in a current of dry carbon dioxide until it becomes black, and all admixed sulphur is expelled. The loss of weight is calculated to the whole quantity and deducted from the weight at 100°.

(*b*) As *oxide* Sb_2O_4, with previous precipitation as sulphide. The sulphide is placed in a porcelain crucible and treated with fuming nitric acid boiling at 86° until completely oxidised, the excess of acid expelled, and the residue heated with partial exposure to air until the weight is constant. The sulphide may also be mixed with 30 to 50 times its weight of precipitated mercuric oxide and heated cautiously until of constant weight. A deep capacious crucible with a lid having a side tube for the exit of vapours has been devised for this and similar estimations.

For a method of estimating small quantities of antimony, as in urine, *see* Schidrowitz and Goldsbrough (Analyst, 1911, 36, 101); Beam and Freak (*idem.* 1919, 44, 196).

Arsenic.

(*a*) As *trisulphide* As_2S_3, which is dried at 100°. The dry precipitate should volatilise completely when heated.

(*b*) As *pentasulphide* As_2S_5. The arsenic is oxidised to arsenic acid by chlorine in alkaline solution, and the precipitation then effected in warm acid solution after decomposing all the chlorate (Brauner and Tomicek, Monatsh. 1887, 8, 642; and Neher, Zeitsch. anal. Chem. 1893, 32, 45).

(*c*) Arsenic acid is estimated as *magnesium pyroarsenate* $Mg_2As_2O_7$, in the same way as phosphoric acid (*which see*). The filter paper is moistened with a solution of ammonium nitrate and dried before burning, in order to prevent reduction (*v.* Ducru, Compt. rend. 1900, 131, 886; *cf. also* Friedheim and Michaelis, Zeitsch. anal. Chem. 1895, 34, 505).

Or the ammonium magnesium arsenate precipitate after washing with dilute ammonia, then with alcohol to remove free ammonia, is titrated with N/2-acid, using methyl-orange as indicator. Each c.c. of N/2-acid is equivalent to 0·01875 gram of arsenic.

Barium.

(*a*) As *sulphate* $BaSO_4$, by precipitation with sulphuric acid (*v. Sulphuric acid*).

(*b*) As *carbonate* $BaCO_3$, which may be dried at a temperature below dull redness after moistening the filter ash with ammonium carbonate (*v. General Methods of Estimation*).

(*c*) As *silicofluoride* (*v. Methods of Separation*).

(*d*) As *bromide* (Thorne, Zeitsch. anal. Chem. 1905, 43, 308).

Bismuth.

(*a*) As *oxide* Bi_2O_3, after precipitation with a slight excess of ammonium carbonate. In presence of chlorides or sulphates the precipitate will contain basic chloride or sulphate, and in this (or in any other) case the bismuth may be precipitated as sulphide, which is oxidised in the crucible by fuming nitric acid boiling at 86°, and then heated.

(*b*) As *sulphide* Bi_2S_3, which is dried at 100° and weighed at intervals of 20-30 minutes. The weight first decreases owing to loss of water, and then increases owing to oxidation; the minimum weight is taken as correct.

(*c*) As *metallic bismuth*. Bismuth is precipitated as metal by adding to slightly acid solutions of its salts, formaldehyde and excess of caustic soda, boiling and filtering through a Gooch crucible, the precipitate being washed with alcohol and dried at 105° (Vanino and Treubert, Ber. 1898, 31, 1303).

(*d*) Other methods: *phosphate* (Stahler and Scharfenberg, Ber. 1905, 38, 3862), *double molybdate* $(Bi(NH_4)(MoO_4)_2$ (Miller and Cruser, J. Amer. Chem. Soc. 1905, 27, 16); and benzildioxime (Atack) (*cf.* Strebinger, Chem. Zeit. 1918, 42, 242).

Cadmium.

(*a*) As *sulphide* CdS, which is dried at 100°, or dissolved in hydrochloric acid, and the solution evaporated to dryness with sulphuric acid, the residue gently ignited and weighed as $CdSO_4$.

(*b*) As *oxide*, after precipitating as basic carbonate from boiling solutions by potassium (not sodium) carbonate and collecting in a Gooch crucible (Amer. J. Sci. 1906, 20, 456).

Calcium.

(*a*) As *oxide* CaO, after precipitation with ammonium carbonate or ammonium oxalate (*v.* Utz, Oest. Chem. Zeit. 1904, 7, 510). In the latter case the solution is made alkaline with ammonia, heated to boiling, and mixed with excess of ammonium oxalate. The precipitate is washed with hot water, and strongly heated until its weight is constant.

(*b*) As *sulphate* $CaSO_4$, by igniting the carbonate or oxalate with pure sulphuric acid; or by heating it with a mixture of ammmonium sulphate and chloride (Willis and Macintire, Analyst, 1918, 102).

Cerium. *V.* Brinton and James, J. Amer. Chem. Soc. 1919, 41, 1080.

Chromium (in chromic salts).

(*a*) As *oxide* Cr_2O_3, after precipitation by ammonia, or better, ammonium sulphide; or by potassium iodide and iodate (Stock and Massaciu, Ber. .1901, 34, 467). When precipitated as chromic hydroxide and weighed after ignition as chromic oxide, care should be taken to avoid oxidation. Ignition in a Rose crucible in a current of hydrogen gives exact results.

(*b*) As *phosphate*, in the same way as aluminium.

Chromium (in chromic acid and chromates).

(*a*) As *oxide* Cr_2O_3. The solution is neutralised, heated to boiling, and mixed with excess of a neutral solution of mercurous nitrate free from nitrous acid. The precipitate is washed with hot water containing mercurous nitrate, and heated to redness in a porcelain crucible until all mercurial vapours are expelled. The mercurous chromate yields chromic oxide.

(*b*) As *chromate*, by precipitation with barium chloride in acetic acid solution (*cf.* Winkler, Zeitsch. angew. Chem. 1918, 31, 46).

Cobalt.

(*a*) As *metallic cobalt*, after precipitation as cobaltic hydroxide by caustic soda or potash with bromine. The solution must be free from ammonium salts, or all ammonia must be expelled by boiling. The precipitate retains traces of alkali, and in accurate estimations the reduced metal should be washed with water, dried, and again heated in hydrogen.

(*b*) As *sulphate* $CoSO_4$, after precipitation as sulphide, which is treated with nitric acid and then with sulphuric acid. If the heated sulphate is at all black, it must be treated again with sulphuric acid.

Copper.

(*a*) As *cuprous sulphide* Cu_2S, using Rose's method, with previous precipitation as cupric sulphide by hydrogen sulphide or sodium thiosulphate (Chem. Zeit. 1895, 19, 1591).

(*b*) As *oxide*, after precipitation by caustic potash or soda in absence of ammonium salts.

(*c*) As *cuprous thiocyanate* CuCNS (Rivot, Compt. rend. 1854, 38, 868; also Amer. J. Sci. 1902, 13, 20 and 138). The warm solution, which must contain no free nitric acid, is slightly acidified with hydrochloric acid, and mixed gradually with an excess of a moderately strong solution of equal parts of ammonium or potassium thiocyanate and ammonium hydrogen sulphite. When cold, the precipitate is collected in a weighed Gooch crucible, washed with cold water and 20 p.c. alcohol, and dried at 110°–120°. The precipitate may also be converted into cuprous sulphide by Rose's method. Cuprous thiocyanate is not quite insoluble, especially in presence of much free acid.

Copper salts are reduced by hypophosphorous acid, or alkaline hypophosphites on warming, and the reduced copper may be washed, dried, and weighed (Dallimore, Windisch).

Glucinum.

As *oxide* GlO, with previous precipitation in the cold by slight excess of ammonia or ammonium sulphide in presence of ammonium chloride, but not caustic soda or potash, or ammonium carbonate. The *basic acetate of glucinum* $[GlO_4(CH_3CO_2)_3]$ is readily soluble in chloroform, and can be distilled unchanged.

Gold.

As *metallic gold*. Nitric acid is removed by evaporation with hydrochloric acid. The solution is acidified with hydrochloric acid, mixed with a large excess of ferrous sulphate solution, and heated gently for a few hours; or it is acidified with sulphuric acid, mixed with oxalic acid, and allowed to stand in a warm place for several hours. Formaldehyde and hydrogen peroxide in alkaline solution can be used as precipitants (Ber 1899, 32, 1968). Nitrous acid is also suggested (Jameson, J. Amer. Chem. Soc. 1905, 27, 1444). The precipitate is collected on a weighed filter, washed and dried.

Iron.

(*a*) As *ferric oxide* Fe_2O_3, after precipitation by ammonia, caustic potash or soda, potassium iodide and iodate (*v. Chromium*), or as basic carbonate, basic acetate or formate. The oxide is heated to redness until its weight is constant; if heated at a higher temperature, it is partially converted into ferroso-ferric oxide Fe_3O_4.

(*b*) Ferrous and ferric salts can be separated and estimated gravimetrically by means of barium carbonate and ammonium chloride, when the ferric salt is decomposed, precipitating ferric hydroxide, and the ferrous salt remains in solution.

Lead.

(*a*) As *sulphate* $PbSO_4$. The solution, which should not be dilute, is mixed with dilute sulphuric acid and twice its volume of alcohol, and allowed to stand, and the precipitate washed with alcohol. If the addition of alcohol is inadmissible, the solution is evaporated with a large excess of dilute sulphuric acid, till fumes are evolved. The residue is taken up with cold water and quickly filtered on a Gooch crucible; and the precipitate is washed with dilute sulphuric acid and afterwards with alcohol to remove all free acid.

(*b*) As *sulphide* PbS, by hydrogen sulphide and Rose's method.

(*c*) As *oxide* PbO, after precipitation by ammonium carbonate, avoiding an excess of ammonium salts.

(*d*) As *metal*.

(*e*) Other methods. As *chromate* and *iodate*.

Magnesium.

(*a*) As *pyrophosphate* $Mg_2P_2O_7$. The solution is mixed with ammonium chloride in sufficient quantity to prevent precipitation by ammonia, made strongly alkaline with ammonia, and then mixed with excess of sodium phosphate, or, better, ammonium phosphate or microcosmic salt. Care should be taken to avoid rubbing or scratching the sides of the vessel. The liquid is allowed to remain for a few hours, filtered, and the precipitate washed with a mixture of strong ammonia (1 part) and water (5 parts) until the washings give only a faint opalescence with silver nitrate after acidifying with nitric acid. The precipitation of the double phosphate is greatly accelerated and a granular non-adherent product obtained by shaking the mixed solutions in a stoppered cylinder. The precipitate is dried, *cautiously* heated in a platinum crucible until all ammonia is expelled, and then heated to redness until the weight is constant. If the precipitate is black, owing to partial reduction, it is moistened with a few drops of strong nitric acid, and again heated until perfectly white.

(*b*) As *oxide* MgO, after precipitation as hydroxide by barium hydroxide, or mercuric oxide, or as double carbonate $MgCO_3(NH_4)_2CO_3$ (Zeitsch. anorg. Chem. 1908, 58, 427), the precipitate being strongly ignited (*v.* Zeitsch. anorg. Chem. 1901, 26, 347).

(*c*) As *pyroarsenate* (*v. Pyrophosphate*, and Amer. J. Sci. 1907, 23, 293).

Manganese.

(*a*) As *sulphide* MnS, by Rose's method after precipitation by ammonium sulphide.

(*b*) As *oxide* Mn_3O_4, after precipitation by sodium carbonate, or ammonium carbonate (Tamm, Zeitsch. anal. Chem. 1872, 11, 425). The hydrated peroxide precipitated by bromine and ammonia, on prolonged ignition yields Mn_3O_4.

(*c*) As *pyrophosphate* $Mn_2P_2O_7$. Ammonium chloride and microcosmic salt are added in considerable excess to the cold manganese solution followed by a slight excess of ammonia. The mixture is then heated till the precipitate becomes silky and crystalline. After cooling for 30 minutes, the precipitate is collected on the Gooch, washed with very dilute ammonia, and ignited (Gooch and Austin, Amer. J. Sci. 1898, 6, 150).

(*d*) As *sulphate* (Gooch and Austin, Amer. J. Sci. 1898, 5, 209).

Mercury (in mercurous compounds).

As *mercurous chloride* Hg_2Cl_2. The dilute cold solution is mixed with a solution of sodium chloride in slight excess, and the precipitate is collected on a weighed filter and dried at 100°.

Mercury (in mercuric compounds).

(*a*) As *sulphide* HgS, which is dried at 100° after precipitation by hydrogen sulphide.

(*b*) As *mercurous chloride* Hg_2Cl_2. The solution is mixed with excess of hydrochloric acid and phosphorous acid (made by allowing phosphorus to oxidise slowly in moist air), and allowed to remain in a warm place for twelve hours. The precipitate is collected on a weighed filter and dried at 100°.

For the estimation of mercury as metal by the dry method, *see* Cumming and Macleod (Chem. Soc. Trans. 1913, 103, 513). For its reduction by zinc filings, *see* Francois (Compt. rend. 1918, 166, 950; Chem. Soc. Abst. 1918, ii. 276).

Molybdenum.

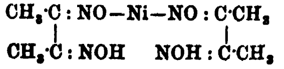
(*a*) As *lead molybdate* $PbMoO_4$. The solution is heated to boiling, mixed with excess of lead acetate, and boiled for a few minutes. The precipitate is washed with hot water, dried at 100°, and heated to low redness in a porcelain crucible.

(*b*) As the *oxide* MoO_3. The solution is neutralised with nitric acid, mixed with excess of a neutral solution of mercurous nitrate, the precipitate washed with mercurous nitrate solution, dried, and heated until the weight is constant. The metal is precipitated as sulphide either in acid solution, or an ammoniacal solution is saturated with hydrogen sulphide and then acidified. The precipitate, collected in a Gooch crucible, is roasted to oxide. The temperature during ignition should not exceed 425°. The conversion of the sulphide into trioxide is complete at 400°; no further change takes place between 400° and 450°, but above 450° the trioxide sublimes. The correct temperature (400°-425°) is most readily attained by using an electric furnace (Wolf, Zeitsch. angew. Chem. 1918, 31, i. 140). Molybdenite is roasted to form trioxide; this is extracted with ammonia, and the filtrate evaporated and residue ignited (Analyst, 1906, 31, 312).

Nickel.

(*a*) As *oxide* NiO, after precipitation as nickelic hydroxide ($Ni(OH)_3$) by caustic potash or soda with the addition of bromine in absence of ammonium salts; or after precipitation by ammonium sulphide thoroughly saturated with hydrogen sulphide, the nickel sulphide being dissolved in aqua regia and the solution precipitated by caustic soda or potash.

(*b*) As *dimethylglyoximate*



$$\begin{array}{l} CH_3{\cdot}C : NO-Ni-NO : C{\cdot}CH_3 \\ \qquad\ | \qquad\qquad\qquad\qquad\quad | \\ CH_3{\cdot}C : NOH \quad NOH : C{\cdot}CH_3 \end{array}$$

(Ni = 20·31 p.c.). A 1 p.c. alcoholic solution of dimethylglyoxime (J. pr. Chem. 1908, 77, 44) is added to a hot dilute hydrochloric acid solution of nickel followed by ammonia in slight excess. The red precipitate, after standing for about an hour, is collected on a Gooch crucible, washed with hot water and dried at 110°–120° (Brünck, Zeitsch. angew. Chem. 1907, 20, 834; *ibid.* 1914, 27, 315).

(*c*) As *nickel dicyanodiamidine* $Ni(N_4H_6C_2O)_2$. Dicyanodiamidine sulphate and caustic alkali are added to an ammoniacal solution of nickel salt, the yellow precipitate collected and dried at 115°. If cobalt is present, hydrogen peroxide is first added to the ammoniacal solution. Aluminium and iron are kept in solution by means of tartaric acid (Grossmann and Schück, Chem. Zeit. 1907, 31, 335, 911).

(*d*) Small quantities of nickel may conveniently be estimated by means of *a-benzildioxime*. For details, *see* Atack (Analyst, 1913, 318). The method is available in presence of cobalt, iron, manganese, zinc, magnesium, and chromium (*cf.* Strebinger, Analyst, 1918, 361).

Platinum.

As *metal*. The solution of platinic chloride free from excess of acid is precipitated by ammonia, or, better, potassium chloride (*v. Potassium*), and the precipitate is filtered by Gooch's method or through a plug of thoroughly dried asbestos contained in a weighed tube The precipitate is dried, heated to redness in a current of hydrogen, washed with water to remove alkaline chloride, again dried, and weighed. The metal is also precipitated by reducing agents (*e.g.* formic acid, alcohol in alkaline solution); and by metals such as magnesium or zinc (Chem. Zeit. 1905, 29, 293).

Potassium.

(*a*) As *platinichloride* K_2PtCl_6. The solution, which must contain the potassium in the form of chloride and be free from acid, is mixed with excess of platinic chloride and evaporated to dryness on the water-bath. The crystalline residue is washed with strong alcohol, without breaking the crystals, until the washings (which at first must be orange, showing the presence of excess of platinum) are colourless. The precipitate is left in the evaporating dish, and the washings are poured through a small filter. When washing is complete, the precipitate is transferred to a weighed porcelain crucible by means of a jet of alcohol from a wash-bottle, and the alcohol is decanted off through the filter. The precipitate in the crucible is dried first at 70° till most of the alcohol is expelled, and then at 100° for half an hour. The filter is dried, and any precipitate is detached from the paper as far as possible and added to the contents of the crucible, which is then weighed. The filter is burnt, and the ash allowed to fall into the crucible, which is again weighed. The increase in weight is filter ash and metallic platinum. The amount of platinichloride corresponding with the latter is calculated and added to the weight of the precipitate (*v.* J. Amer. Chem. Soc. 1895, 17, 453; and Zeitsch. anal. Chem. 1906, 45, 315; Chem. Zeit. 1906, 30, 684). Or the precipitate of platinichloride is collected, washed with alcohol-ether water mixture, then dissolved in boiling water, and the solution boiled with an excess of sodium formate; after a few minutes hydrochloric acid is added, the heating continued until the reduced platinum has flocculated, when the platinum is collected, washed, ignited, and weighed (Steel, Analyst, 1918, 43, 348).

(*b*) As *perchlorate* $KClO_4$. The solution containing potassium and sodium as chlorides is evaporated down with excess of dilute perchloric acid until all the hydrogen chloride is expelled. The residue is taken up with alcohol, the precipitate collected on a Gooch crucible, washed with alcohol, and dried at 130° (Amer. J. Sci. 1897, 2, 263; *cf.* Davis, Analyst, 1913, 38, 47; Thin and Cumming, Trans. Chem. Soc. 1915, 107, 361; Baxter and Kobayashi, J. Amer. Chem. Soc. 1917, 39, 249; Gooch and Blake, Amer. J. Sci. 1917, 44).

As *cobaltinitrite*. The solution is evaporated and the residue mixed with 3 c.c. of a 50 p.c. cobaltous chloride solution and 3 c.c. of a 50 p.c. sodium nitrite solution, and, after stirring, mixed with 2 c.c. 50 p.c. acetic acid. After standing the precipitate is collected on a filter, washed, and treated in a beaker with excess of N/50 potassium permanganate, warmed, 15 c.c. sulphuric acid (1 : 1) added, and the excess of permanganate titrated with oxalic acid solution. The precipitate has the formula $K_2CoNa(NO_2)_6$, and according to theory, 1 c.c. of N/50 permanganate = 0·000156 gram K_2O; experiment shows a better factor is 0·000172 (Van der Horn van der Bos, Analyst, 1913, 294; *cf.* Mitscherlich and Fischer, Analyst, 1912, 37, 588; Haff and Schwartz, Analyst, 1917, 372). Bennett (Analyst, 1916, 165) combines the two methods by separating the potassium as the cobaltinitrite and weighing it as perchlorate.

Selenium.

As *selenium*. The solution is strongly acidified with hydrochloric acid, mixed with excess of sulphurous acid or sodium hydrogen sulphite, and boiled for about fifteen minutes. The precipitate is collected on a weighed filter and dried at a temperature below 100°. Solutions of selenium containing hydrochloric acid cannot safely be concentrated by evaporation except in presence of a large quantity of alkaline chlorides, which prevent the volatilisation of the selenium as chloride.

Hypophosphorous acid in alkaline solution, and potassium iodide in acid solution, have also been recommended as reducing agents (Zeitsch. anorg. Chem. 41, 448; and Amer. J. Sci. 1896, [4] 1, 416). For a review of methods for estimating selenium, *see* Zeitsch. anorg. Chem. 1904, 41, 291).

Silver.

As *chloride* AgCl, or *bromide* AgBr. The solution is acidified with nitric acid, heated to boiling, and mixed with a slight excess of sodium chloride or potassium bromide. Estimation as bromide is to be recommended, since silver chloride is not quite insoluble in pure water. The precipitate is washed with hot water, dried, detached from the paper as far as possible, transferred to a porcelain crucible, and dried at 150°, or heated slowly until it shows signs of fusion at the edges, and weighed. The filter is burnt and the ash added to the crucible, which is again weighed. The increase in weight is filter ash and metallic silver. The quantity of bromide or chloride corresponding with the latter is calculated and added to the weight of the precipitate.

Sodium is weighed in the form of chloride together with any potassium which may be present, and is estimated by difference, or it may be estimated directly as sulphate or chloride if potassium is absent.

The following reagent precipitates sodium even from very dilute solutions, and is not interfered with by the other alkali metals or by magnesium and the metals of the alkaline earths. Three grams of bismuth nitrate and 30 grams of potassium nitrite are dissolved in water containing sufficient nitric acid to remove any turbidity, about 1·6 grams of cæsium nitrate are added, and the solution diluted with water to 100 c.c. The precipitation should be carried out in a stoppered bottle in an inert atmosphere. The precipitate, $5Bi(NO_2)_3,9CsNO_2,6NaNO_2$, contains 3·675 p.c. sodium (*v.* Ball, Chem. Soc. Trans. 1910, 97, 1408).

Strontium.

(*a*) As *sulphate* $SrSO_4$. The solution, which must contain but little free acid, is mixed with excess of dilute sulphuric acid and at least an equal volume of alcohol, and the precipitate is washed with alcohol. If alcohol cannot be used, a much larger excess of sulphuric acid is added and the precipitate is washed with cold water, but the results are less exact.

(*b*) As *carbonate* $SrCO_3$ (which must not be heated too strongly) after precipitation by ammonium carbonate.

According to Winkler (Zeitsch. angew. Chem. 1918, 31, i. 80), the most convenient and exact method of estimating strontium is to precipitate it as *oxalate* by the addition of a 10 c.c. solution of potassium oxalate and washing with saturated strontium oxalate solution. The precipitate is dried at 100°, and weighed as SrC_2O_4,H_2O, or at 132°, and weighed as SrC_2O_4.

Tellurium.

(*a*) As *tellurium*, by reducing solutions of ellurous or telluric compounds with sulphur ioxide and hydrazine hydrochloride (Lenher, . Amer. Chem. Soc. 1908, 30, 387). Other reducing agents have been employed: sulphur dioxide nd potassium iodide, hypophosphorous acid, nd grape sugar in alkaline solution.

(*b*) As *dioxide* TeO_2 (*v.* Amer. J. Sci. 1909, v.) 28, 112).

Thallium.

(*a*) As *thallous iodide* TlI. The solution is eated with sulphurous acid to reduce all the hallium compounds to thallous salts, allowed to ool, and then mixed with excess of potassium odide. The precipitate is washed with dilute lcohol, and dried on a weighed filter at 170° v. Baubigny, Compt. rend. 1892, 113, 544).

(*b*) As *thallous platinichloride*. This salt is ery insoluble, but is difficult to filter (Crookes, elect Methods, 4th ed. p. 172).

Tin.

As *oxide* SnO_2, which is obtained when tin r one of its alloys is treated with nitric acid. The solution is boiled for ten minutes to ensure omplete precipitation, and the precipitate is igested for an hour with dilute nitric acid 1 : 6) at 100° to remove other metals, washed with hot water, and ignited.

In other cases the tin is precipitated as ydrated oxide. If the solution contains stannous alts, the latter are oxidised by chlorine or by ydrochloric acid and potassium chlorate, ammonia added until a slight precipitate forms, nd hydrochloric acid until the precipitate just redissolves. The solution is then mixed with a moderately large quantity of a strong solution of ammonium nitrate or sodium sulphate, and boiled for some time. The precipitate is washed with hot water by decantation and on the filter, dried, and heated. To ascertain if precipitation is complete, a small quantity of the filtrate is added to a hot solution of ammonium nitrate or sodium sulphate.

If the tin has been precipitated as stannic sulphide, the latter is washed with a solution of sodium chloride, and finally with a solution of ammonium acetate, dried, and roasted in a porcelain crucible until the weight is constant. Decomposition is facilitated by adding a small quantity of ammonium carbonate.

In all cases the filter is burnt separately and the ash dropped into the crucible.

Titanium.

As *dioxide* TiO_2, after precipitation by ammonia. Usually the substance is dissolved in sulphuric acid, or is fused with potassium hydrogen sulphate and dissolved in water. The solution is diluted largely and boiled for some time, when all titanium is precipitated as hydrated oxide, which is rendered anhydrous by ignition. The solution should contain 0·5 p.c. of free sulphuric acid; if less, the precipitate is impure, if more, precipitation is incomplete (Lévy). In presence of iron the results are always somewhat too high.

Baskerville recommends fusing titaniferous iron ores with potassium hydrogen sulphate containing some sodium fluoride. The product is boiled with water containing nitric acid and then neutralised with ammonia. The precipitate is dissolved in dilute hydrochloric acid, avoiding any excess. The liquid is then saturated with sulphur dioxide and boiled, the precipitate being collected, ignited, and weighed as TiO_2 (J. Soc. Chem. Ind. 1900, 19, 419; also J. Amer. Chem. Soc. 1903, 25, 1073; and 1910, 32, 957).

Tungsten.

As *tungstic anhydride* WO_3. The solution containing the tungsten as an alkaline tungstate is neutralised with nitric acid and precipitated with a neutral solution of mercurous nitrate. The precipitate is washed with a solution of mercurous nitrate, dried, and heated in a porcelain crucible, when tungstic anhydride is left.

Fused lead tungstate, when boiled with strong hydrochloric acid, gives a precipitate of tungstic acid (Brearley, Chem. News, 1899, 79, 64).

Uranium.

(*a*) As the *oxide* U_3O_8. The solution, oxidised if necessary by nitric acid, is heated to boiling and mixed with a *slight* excess of ammonia. The precipitate of acid ammonium uranate is washed with ammonium chloride solution, dried, and strongly heated.

(*b*) As the *pyrophosphate* $(UO_2)_2P_2O_7$, obtained by precipitating uranyl ammonium phosphate $(UO_2)(NH_4)PO_4$ with ammonium phosphate in the presence of ammonium acetate and igniting the precipitate at low redness. For the application of this process to uranium minerals, see Low's Technical Methods of Ore Analysis, 3rd ed. p. 223; and J. Amer. Chem. Soc. 1901, 23, 685.

Vanadium.

(*a*) As *barium pyrovanadate* $2BaO{\cdot}V_2O_5$. The solution is neutralised with ammonia, heated to boiling, mixed with excess of barium chloride, agitated, and cooled quickly out of contact with air. The precipitate is washed and heated.

(*b*) As *manganese pyrovanadate* $2MnO\cdot V_2O_5$. The solution is mixed with a slight excess of ammonium chloride and ammonia, manganese chloride or sulphate mixed with ammonium chloride is added in excess, and the liquid is boiled two or three minutes and allowed to cool out of contact with the air. The precipitate, which should be brownish yellow and free from oxidation products, is washed with cold water and heated.

(*c*) As *pentoxide* V_2O_5, obtained (i.) by precipitating barium or lead vanadate, decomposing with sulphuric acid, filtering, evaporating the filtrate, and igniting; (ii.) by precipitating and igniting mercury vanadate; (iii.) by precipitating ammonium vanadate by ammonium chloride and igniting the precipitate.

For other methods of estimating and separating vanadium, *v.* A. Carnot, Compt. rend. 104, 1803 and 1850; Chem. Soc. Abstr. 1887, 896; Chem. Zeit. 1905, 29, 392; Amer. J. Sci. 1910, 30, 220.

Zinc.

(*a*) As *oxide* ZnO, with previous precipitation by sodium carbonate in absence of ammonium salts.

(*b*) As *sulphide* ZnS, by Rose's method after precipitating with ammonium sulphide.

The filtration of the zinc sulphide may be promoted by precipitating in the presence of ammonium acetate or thiocyanate, and washing with a 5 p.c. solution of either of these salts. If mercuric chloride is added to the solution, the mixed precipitate of mercuric and zinc sulphides filters much better than the latter alone; the former is expelled on ignition.

Zirconium.

Zirconium is quantitatively precipitated by ammonium phosphate from solutions which are either neutral or contain up to 20 p.c. of sulphuric acid. The precipitate is calcined and weighed as pyrophosphate, the factor for conversion to ZrO_2 being 0·487. The method may be used for the estimation of zirconium in presence of iron, chromium, and aluminium, but an acidity equal to 20 p.c. sulphuric acid is necessary if the first two are present, or 10 p.c. if only aluminium is present, in order to avoid simultaneous precipitation of these metals (Nicolardot and Reglade, Compt. rend. 1919, 168, 348).

ACID RADICALS.

Carbonic acid.

The estimation of carbon in carbonates may be made by a loss in weight method. The carbonate is weighed into an apparatus fitted with a stoppered dropping funnel containing acid to decompose the carbonate, and an exit tube containing strong sulphuric acid to dry the escaping gas. The apparatus is weighed with the acids, &c., after the carbonate has been introduced. The acid is then allowed to drop on the carbonate until the decomposition is complete, and the liquid boiled to expel dissolved carbon dioxide. The apparatus is again weighed and the loss of weight gives the amount of carbon dioxide. The apparatus is figured in most treatises on quantitative analysis. More accurate results are obtained by weighing the carbon dioxide directly by absorbing it in weighed tubes containing soda lime or in bulbs containing aqueous caustic potash. For a complete form of apparatus for this estimation, *see* Thorpe's Quantitative Analysis, 9th ed. p. 86, and Clowes and Coleman's Analysis, 8th ed. p. 104.

When carbonates and sulphides occur together, the gases evolved on treatment with acid are passed into a solution of copper acetate acidified with acetic acid and heated to boiling. Hydrogen sulphide is absorbed, with formation of copper sulphide, and carbon dioxide passes on.

For a convenient apparatus for determining small quantities of carbon dioxide, *see* Sinnatt (Analyst, 1913, 136). As shown by Morgan a solution of phosphoric acid may conveniently replace the hydrochloric or sulphuric acid usually employed (Proc. Chem. Soc. 1904, 20, 167).

For the estimation of carbon dioxide in the presence of nitrites, sulphides, and sulphites, *see* Marle, Chem. Soc. Trans. 1909, 1491; and Wolkowitz, Zeitsch. angew. Chem. 1894, 165.

Chloric acid.

Any chlorine present as chloride is determined, the chlorate reduced by a zinc-copper couple, and the chlorine again determined. The difference is the amount of chlorine existing as chlorate (Thorpe, Chem. Soc. Trans. 1873, 541). Thin granulated zinc is washed with caustic soda solution, then with dilute sulphuric acid, which is allowed to act for a short time, and finally with water. It is then covered with about 100 c.c. of a 3 p.c. solution of copper sulphate heated to 40°-50°. When most of the copper has been deposited, the liquid is carefully poured off, and treatment repeated with a fresh quantity of solution. The zinc-copper couple is now very carefully washed with distilled water by decantation, not more than 0·5 gram of potassium chlorate, or the equivalent quantity of any other chlorate, is weighed out into the beaker and dissolved in about 25 c.c. of warm water, which should just cover the couple. The liquid is heated gently for half an hour, then boiled for half an hour, dilute sulphuric acid added drop by drop until the white precipitate of zinc hydroxide and oxychloride just dissolves, filtered, the filtrate neutralised with pure calcium carbonate, and the chlorine estimated by standard silver nitrate solution (Chem. Soc. Trans. 1888, 166).

This reduction may also be effected by Devarda's alloy (Al 45, Zn 5, Cu 50). Jannasch recommends hydroxylamine sulphate and excess of nitric acid as a suitable reducing agent for chlorates while bromates and iodates are best reduced by hydroxylamine in ammoniacal solution (Ber. 1905, 38, 1576). Formaldehyde in dilute nitric acid reduces chlorates in 30 minutes and bromates in 2½ hours; iodates are not reduced (Grützner. Arch. Pharm. 1896, 294, 634; compare Brunner and Mellet, J. pr. Chem. 1908, 77, 33).

Hydrobromic, hydrochloric, and hydriodic acids.

As silver salts (AgBr, AgCl, AgI). The solution is mixed with excess of silver nitrate, acidified with nitric acid, and heated to boiling. The precipitate is treated exactly as in the estimation of silver.

Hydrofluoric acid.

(*a*) As *calcium fluoride* CaF_2, in the case of soluble fluorides. The solution is mixed with a moderate excess of sodium carbonate, heated to boiling, and mixed with excess of calcium chloride. The precipitate is washed, dried, and heated to redness in a platinum crucible, then treated with excess of acetic acid, evaporated to dryness, and heated to expel excess of acid. The product is now heated with water, and the insoluble calcium fluoride filtered off, washed, and heated.

(*b*) Indirectly as *silicon fluoride* SiF_4. The finely powdered solid substance is placed in a deep platinum crucible and covered with three or four times its weight of pure precipitated silica, the weight of which is accurately known. Sulphuric acid is then added, and the crucible gently heated for half an hour. The temperature is raised to expel most of the sulphuric acid, the residue treated with hydrochloric acid, washed, dried, and heated. The hydrofluoric acid is calculated from the loss in weight of the silica: $4HF = SiO_2$. The amount of silica in the substance must be known, and its weight added to that of the admixed silica.

(*c*) By *distillation and weighing as calcium fluoride.* The fluoride is decomposed by concentrated sulphuric acid in a platinum apparatus; the hydrogen fluoride carried off in a current of air and carbon dioxide and absorbed in a solution of pure caustic soda contained in a platinum dish. Calcium chloride is added to this solution and the precipitate ($CaCO_3$ and CaF_2) washed, ignited, and treated with dilute acetic acid in moderate excess. After evaporation to expel this excess of acid, the residue is taken up with water and the insoluble calcium fluoride collected, washed, and ignited (Jannasch and Röttgen, Zeitsch. anorg. Chem. 1895, 9, 267). The apparatus employed is figured in Jannasch's Praktischer Leitfaden der Gewichtsanalyse, 2nd ed. 411 (compare also J. Amer. Chem. Soc. 1901, 23, 825; and Chem. News, 1905, 92, 184).

(*d*) Directly as *silicon fluoride* (Fresenius). The mineral is finely powdered and intimately mixed with ignited quartz and heated with concentrated sulphuric acid in a dry U-tube at 150°–160°. A current of dry air free from carbon dioxide is drawn through the decomposition tube and thence through a series of five U-tubes. The first of these is empty and cooled by immersion in cold water; the second contains glass-wool, or, if the substance contains chlorine, half is filled with pumice impregnated with anhydrous copper sulphate, and the other half with pure dry calcium chloride. The third and fourth tubes are weighed and serve to absorb the silicon fluoride; the third contains pumice moistened with water, and the fourth contains soda lime and calcium chloride. The fifth tube is a guard tube containing the same reagents as the fourth. After one or two hours the decomposition of the fluoride is complete, and the gain in weight of the absorption tubes represents the amount of silicon fluoride generated. This process may be rendered volumetric (*v. Volumetric section*).

Hydrogen sulphide (sulphides).

Insoluble sulphides are decomposed by hydrochloric acid in a flask similar to that used in the gravimetric estimation of carbonic acid, and the gas evolved is led into two or three bulb U-tubes containing a solution of bromine in dilute hydrochloric acid, which converts the hydrogen sulphide into sulphuric acid. When decomposition is complete, the liquid in the flask is boiled, and the last traces of the gas are drawn through the bulbs by means of an aspirator. The contents of the bulb tubes are transferred to a beaker, heated to expel bromine, and the sulphuric acid precipitated by barium chloride.

Sulphides which are not decomposed by hydrochloric acid may be oxidised with aqua regia, hydrochloric acid and bromine, or hydrochloric acid and potassium chlorate, the sulphuric acid formed being weighed as barium sulphate.

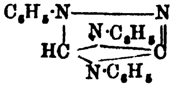
Nitric acid.

(*a*) Indirectly, as ammonia, by means of the zinc-copper couple (Thorpe). A zinc-copper couple (*v. Chloric acid*) is made in a flask into which is weighed a quantity of the nitrate corresponding with not more than 0·5 gram of potassium nitrate, and sufficient water is added to just cover the couple. The flask is attached to a condenser, the other end of which is connected with a U-tube or flask containing hydrochloric acid, as in the estimation of ammonia. The liquid is gently heated for some time, and then distilled nearly to dryness. After cooling, a further quantity of water is added to the couple, and distillation repeated. The ammonia in the distillate is estimated as platinichloride, or is received in a measured volume of standard acid and titrated. The reduction can also be conveniently effected by the use of Devarda's alloy (*v. Chloric acid*) in alkaline solution (Analyst, 1910, 35, 307).

(*b*) *Schloesing's method.* When a solution of a nitrate is heated with an acid solution of a ferrous salt, the nitrate is decomposed, the whole of the nitrogen being evolved as nitric oxide, which is measured. The difficulty lies mainly in obtaining the nitric oxide free from air. The apparatus employed consists of a *small* distilling flask provided with a side tube which terminates under a gas-collecting tube in a mercurial trough. The neck of the flask is fitted with a cork, which carries a tube funnel provided with a stop-cock and another tube connected with a carbon-dioxide apparatus. Carbon dioxide *free from air* is passed into the apparatus until all air is expelled and the gas issuing from the exit tube is completely absorbed by caustic potash. The substance containing the nitrate, which must be in the solid condition, is dissolved in 2 or 3 c.c. of concentrated ferrous chloride solution, mixed with 1 c.c. of strong hydrochloric acid, and introduced into the flask by means of the funnel tube, care being taken that no air enters. The dish and the funnel are rinsed with very small quantities of acid, the object being to use as little liquid as possible. The contents of the flask are then rapidly boiled to dryness, the evolved gas being collected in the tube over mercury, and carbon dioxide is driven through the apparatus to expel all nitric oxide. The mixture of nitric oxide and carbon dioxide is transferred to an apparatus for gas analysis; the latter absorbed by caustic potash, and the former mixed with oxygen and absorbed by alkaline pyrogallol. Nitrites are converted into nitrates by addition of hydrogen peroxide during evaporation of the original solution (*v.* Warington, Chem. Soc. Trans. 1880, 468, and 1882, 345).

(c) *By standard indigo solution* (Warington, Chem. News, 35, 45, and Chem. Soc. Trans. 1879, 578).

(*d*) **As** 1 : 4-*diphenyl*-3 : 5-*endanilodihydrotriazole nitrate* $C_{20}H_{16}N_4,HNO_3$. A 10 p.c. solution of the base 1 : 4-diphenyl-3 : 5-endanilohydrotriazole 'Nitron,'



in 5 p.c. acetic acid produces a voluminous white precipitate in dilute nitric acid or nitrate solution. Nitrites interfere by giving a sparingly soluble salt with this base; they are removed by hydrazine sulphate. Bromides, iodides, chlorates, perchlorates, and chromates, are also precipitated by nitron, and must be removed. Organic matters do not seriously affect the method, which has been tested successfully with solutions containing 0·5 p.c. of gelatine, and 2 p.c. of dextrin (Busch, Ber. 1905, 38, 861). The method gives favourable results for nitrates in water or fertilisers (Collins, Analyst, 1907, 32, 349).

(*e*) Howard and Chick have shown that cinchonamine gives a very insoluble nitrate and can be used in estimating nitric acid and its salts (J. Soc. Chem. Ind. 1909, 28, 53).

Oxalic acid.

As *calcium oxalate*. The method is already indicated under *Calcium*.

Phosphoric acid.

As *magnesium pyrophosphate* $Mg_2P_2O_7$. The operation is conducted as in the estimation of magnesium. If magnesium sulphate is used as the precipitant, the precipitate may be contaminated with basic magnesium sulphate; it is therefore advisable to employ a solution of the chloride, which is made as follows: 85 grams of crystallised magnesium sulphate are dissolved in boiling water, acidified with 5 c.c. of hydrochloric acid, mixed with an aqueous solution of 82 grams of crystallised barium chloride, boiled, and filtered. A few drops of magnesium sulphate solution are added to be sure that there is no excess of barium, then 165 grams of pure ammonium chloride, and 260 c.c. of ammonia, and the solution diluted to 1 litre. After two or three days the solution is filtered. In many cases the phosphoric acid is first separated by ammonium molybdate (*v. Methods of separation*).

Silicic acid.

As *silica* SiO_2. Soluble silicates are acidified with hydrochloric acid and evaporated to complete dryness; moistened with strong hydrochloric acid, again evaporated twice to dryness, so as to agglomerate the silica, the residue treated with dilute acid, and the insoluble silica washed with hot water and ignited.

Insoluble silicates are very finely powdered, intimately mixed with about five times their weight of a dry mixture of sodium and potassium carbonates in equal proportions, and heated to redness in a platinum crucible for half an hour. The cooled mass is treated with water, acidified with hydrochloric acid, and evaporated as above.

(For the separation of silica when the alkalis have to be estimated, *v. Methods of separation*, Group VI.)

Sulphuric acid.

As *barium sulphate* $BaSO_4$, by precipitation with barium chloride. The chief difficulty arises from the tendency of the barium sulphate to separate in a finely divided condition and to carry down impurities, especially in presence of nitrates and potassium salts. These sources of error are avoided by taking care that the solution is somewhat dilute, is free from nitrates, and contains a moderate but not excessive quantity of free hydrochloric acid. The solution and the barium chloride solution should both be heated to boiling, and mixed *gradually, with continual agitation*. The liquid may be filtered as soon as it has become clear, and the precipitate is washed with hot water and heated to dull redness. If too little hydrochloric acid is present, the precipitate is liable to be impure; if a very large excess of the acid is present, precipitation is not quite complete (compare Allen and Johnston, J. Amer. Chem. Soc. 1910, 32, 588).

Sulphurous acid.

Indirectly as barium sulphate after oxidation by bromine water, excess of bromine being expelled by boiling.

Thiosulphuric acid.

Indirectly as barium sulphate after oxidation by bromine water, excess of bromine being expelled by boiling.

Water is usually estimated by difference. If a direct determination is required, the method to be adopted will depend upon circumstances. In many cases it is sufficient to heat the substance on a watch-glass, or in a crucible in a drying oven, at a definite temperature, until the weight is constant. During weighing the dried substance must be carefully protected from the air. Attention must, however, be paid to the possibility of the volatilisation of substances other than water. Many hydrated haloid salts, for example, lose part of their acid. In such cases the substance is previously mixed with a known weight of perfectly dry lead monoxide. Ammonia, ammonium salts, and volatile organic matter may also be given off. If the drying is conducted in a glass tube, the vapours may be led into standard acid and the ammonia determined by titration: the total loss, *minus* the ammonia, gives the amount of water. Some substances increase in weight in consequence of oxidation. Frequently it is desirable to collect the evolved water and weigh it directly. The substance is introduced into a glass tube (plain, or with a bulb in the middle) drawn out and bent at right angles at one end, which passes directly, without any intervening indiarubber tube, through the cork of a U-tube containing either calcium chloride or pumice moistened with strong sulphuric acid (*v.* ORGANIC ANALYSIS).

In certain cases the water may frequently be estimated with considerable accuracy by boiling the substance with paraffin oil and measuring the expelled water in a graduated tube (*cf.* Huntly and Coste, J. Soc. Chem. Ind. 1913, 32, 62; Campbell, *ibid.* 1913, 32, 67; Skertchley, *ibid.* 70; St. von Haydin, Analyst, 1913, 177; Michel, Analyst, 1913, 207).

All fluosilicates, even topaz, evolve silicon fluoride on ignition, and water is estimated by mixing the mineral with lead oxide in a hard glass tube, heating the mixture in a current of dry air and passing the gases over a layer of lead oxide contained in the same tube. The water is collected and weighed in calcium chloride tubes

Methods of Separation.

A. *The Estimation of the Metals in their Ores and Alloys.*

In this section the metals are arranged in the order in which they occur in the qualitative groups. Both gravimetric and volumetric methods are included in this description, the latter being indicated wherever possible, owing to the greater rapidity with which the analysis can be executed.

Group I.

Silver is separated from all other metals by treating its ores and alloys with moderately strong nitric acid, evaporating off excess of solvent, diluting with water, and adding to the filtered solution either hydrochloric acid or sodium chloride. To remove any lead or thallous chloride which may be present, the precipitate is extracted repeatedly with warm water; it should, however, be remembered that silver chloride is not absolutely insoluble in hot water. Silver is conveniently estimated volumetrically in the above dilute nitric acid solution, after boiling off nitrous fumes, by adding ferric indicator and titrating with standard ammonium thiocyanate in accordance with Volhard's method (*see Volumetric section*). The presence of other metals having colourless salts does not interfere with this process; nickel, cobalt, and copper must not be present to any large extent, and mercury should be absent because of the insolubility of mercuric thiocyanate. When more than 60 p.c. of copper is present, the silver is precipitated with excess of alkali thiocyanate. The well-washed silver thiocyanate is decomposed by strong nitric acid, the sulphuric acid produced precipitated by barium nitrate, and the Volhard titration effected without filtering off the barium sulphate (*v.* Ber. 1905, 38, 566).

The silver in argentiferous galena is estimated by fusing the sulphide with crude potassium hydrogen tartrate (argol), and sodium carbonate in an iron crucible, and by heating the lead-silver button thus obtained in a porous bone-ash crucible ('cupel') until the lead is removed as oxide, partly by volatilisation and partly by absorption into the cupel. The residual silver is detached from the cold cupel and weighed.

Gold quartz is assayed for silver by heating the mineral with lead oxide, and a reducing flux, when the lead produced extracts both the gold and silver. This alloy is cupelled, and the silver-gold button is 'parted' by heating with strong nitric acid diluted with three parts of water; the residual gold is collected, ignited, and weighed. The silver is precipitated by hydrochloric acid from the nitric acid solution. When more than 30 p.c. of gold is present in the button before parting, this metal will retain silver. In order to prevent this retention, a known weight of silver is added to the fused button. (For further details of the separations of gold, silver, and lead in the dry way, see Assaying.)

Thallium, in the more stable thallous condition to which thallic salts are readily reduced, is separated from the metals of Group II. by precipitating the latter with hydrogen sulphide in acid solution. Alkali hydroxides separate it from all metals, giving insoluble hydroxides, and ammonium sulphide, which precipitates thallous sulphide, separates this metal from the alkalis and alkaline earths. Gravimetrically, thallium can be weighed as acid sulphate $TlHSO_4$, stable at 240°, and as sulphate Tl_2SO_4, stable at low red heat; it can be precipitated and weighed as iodide TlI, platinichloride Tl_2PtCl_6, and chromate Tl_2CrO_4. Volumetrically, it can be estimated by the oxidation of thallous salts by permanganate or by titrating with thiosulphate the iodine set free in accordance with the following reaction: $TlCl_3 + 3KI = TlI + 3KCl + I_2$ (Chem. Soc. Proc. 1908, 24, 75).

Group II.

Mercury in its ores is generally estimated by distillation with quicklime in a current of coal gas or carbon dioxide. The decomposition of the mercury compounds is facilitated by mixing copper strips with the quicklime, and the presence of this reducing agent is essential in the case of mercuric iodide. The mercury which distils over is collected under water, washed, dried, and weighed. Ores containing only small amounts of mercury are decomposed by heating with iron filings in a porcelain crucible, *a*, having a silver lid, *f*, which is cooled by a water-jacket, *b*, laid upon it. The mercury condenses on the under surface of the silver plate, *f*, which is weighed before and after the experiment (*v.* Holloway, Analyst 1906, 31, 66).

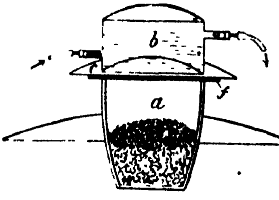


Fig. 8.

Mercury is separated from all other metals in the wet way by dissolving the ore or alloy in nitric acid or aqua regia, diluting considerably, precipitating the sulphides of Group II. by hydrogen sulphide, removing the arsenic-tin sub-group by means of yellow ammonium sulphide (*not* sodium sulphide or hydroxide), treating the residual sulphides with dilute nitric acid (sp.gr. 1·2–1·3), and dissolving the final residue in aqua regia and filtering if necessary from sulphur and lead sulphate. The mercury can be reprecipitated by almost neutralising the acid solution, adding in succession ammonium sulphide, caustic soda and ammonium nitrate. The caustic soda redissolves the sulphide initially formed as the soluble double sulphide $Hg(SNa)_2$, and from this the ammonium nitrate reprecipitates mercuric sulphide in a form suitable for collection. The precipitate is washed successively with water, alcohol, and carbon disulphide, dried at 110°, and weighed as HgS. (For other methods of separating mercury, see Jannasch, Zeitsch. anorg. Chem. 1896, 12, 132, and 359; and Stähler, Chem. Zeit. 1907, 31, 615.)

Lead in its ores and alloys is usually separated from other metals by dissolving the substance in hydrochloric or nitric acid, or if necessary in a mixture of the two acids and evaporating down the solution with sulphuric acid until white fumes are evolved. The mixture is then cooled diluted with water, and the lead sulphate quickly collected. If the amount of lead is small, alcohol must be added to complete the precipitation. The lead sulphate thus obtained is freed from silica, stannic oxide, and other impurities by dissolving it in an excess of ammonium or sodium acetate.

When separated as lead sulphate, the lead can be estimated volumetrically by boiling the precipitate with ammonium carbonate and then dissolving the lead carbonate in acetic acid. The lead is thus converted into lead acetate which is titrated with standard ferrocyanide using as indicator drops of uranium acetate on a porcelain plate. The lead may also be reprecipitated as oxalate from the acetate solution by alkali oxalate, the washed lead oxalate being then suspended in dilute sulphuric acid, and titrated with standard permanganate. From the solution of the sulphate in sodium acetate the lead can be precipitated as chromate by potassium dichromate. The chromate is dissolved in dilute nitric acid, and reduced with methyl or ethyl alcohol. The solution, rendered ammoniacal, is treated with oxalic acid, when lead is precipitated and titrated as above with standard permanganate (*v.* Chem. News, 1896, 73, 18; J. Amer. Chem. Soc. 1896, 18, 737; Zeitsch. anal. Chem. 1902, 41, 653). Lead may be separated from copper by electrolysing a solution of the metals in dilute nitric acid with a weak current (0·5–1·5 amperes and 1·4 volts), when the lead is precipitated as dioxide on the anode (a platinum dish with unpolished inner surface).

Bismuth is separated from all other metals but those of Group II. by the precipitation of its sulphide by hydrogen sulphide in acid solution. The insolubility of the sulphide in ammonium sulphide separates this metal from arsenic, antimony, and tin. The further separation of bismuth from mercury, copper, and cadmium presents no particular difficulty, and is effected by taking advantage of the solubility of bismuth sulphide in nitric acid (sp.gr. 1·25), and the precipitation of bismuth oxychloride on diluting considerably an acid solution of bismuth chloride. The problem of separating bismuth from lead is, however, much more troublesome, and the following appear to be most trustworthy methods: (i.) the separation of the bismuth as basic nitrate and the solution of lead nitrate in dilute ammonium nitrate (J. pr. Chem. 1858, 74, 345); (ii.) the distillation of the mixed sulphides in a current of bromine, when bismuth bromide is volatilised, leaving behind lead bromide (Jannasch, Praktischer Leitfaden der Gewichtsanalyse, 1st ed. 155); (iii.) the precipitation of bismuth as the basic formate; a repetition of this operation gives a precipitate free from lead, which is dissolved in dilute nitric acid, the solution almost neutralised with sodium carbonate, and the bismuth then finally precipitated and weighed as phosphate $BiPO_4$ (Stähler, Chem. Zeit. 1907, 31, 615). The lead in the filtrate from the formate separation is precipitated as sulphide, converted into sulphate, and weighed as such. This method of separation gives accurate results (Little and Cahen, Analyst, 1910, 35, 301).

Copper is separated from the metals of Groups III., IV., V., and VI., by precipitation as sulphide by hydrogen sulphide in acid solution. In alloys and ores it is generally separated from antimony and tin by rendering these insoluble by the action of moderately strong nitric acid. If, however, the sulphides of these metals and arsenic are present, they are extracted from the precipitate with alkali sulphides (not ammonium sulphide). The insoluble residue, containing the sulphides of copper, bismuth, lead, mercury, and cadmium, is treated with nitric acid (*v. Mercury* and *Bismuth*). Copper is readily separated from bismuth by means of ammonium carbonate, which precipitates basic bismuth carbonate, leaving copper in solution. The separation from cadmium may be effected by one of the following methods:—(1) Hydrogen sulphide is passed into a boiling solution of the sulphates of copper and cadmium in dilute sulphuric acid (1 : 4). The precipitated copper sulphide, which contains some cadmium, is redissolved in nitric acid, and, after expelling excess of the solvent, the precipitation is repeated. (2) The copper is precipitated as cuprous thiocyanate, leaving cadmium in solution. (3) The copper is converted into potassium cuprocyanide $K_3Cu(CN)_4$, with a considerable excess of potassium cyanide, and the cadmium precipitated with hydrogen sulphide or ammonium sulphide (compare also Browning, Amer. J. Sci. 1893, [3] 46, 280).

The following volumetric processes for copper are employed in the technical analysis of the ores of this metal. (i.) The mineral is dissolved in hydrochloric and nitric acids, and the solution boiled down with sulphuric acid to expel the volatile acids. The copper is precipitated from the boiling solution by introducing a sheet of aluminium and redissolving in nitric acid with the addition of bromine to destroy nitrous fumes. The solution is neutralised with ammonia, acidified with acetic acid, and treated with excess of potassium iodide, when the liberated iodine is titrated with standard thiosulphate (Low, J. Amer. Chem. Soc. 1902, 24, 1082). (ii.) A solution of potassium cyanide is standardised against pure copper foil by dissolving the latter in nitric acid, adding bromine, boiling to expel nitrous fumes and excess of bromine, adding ammonia till strongly alkaline, and titrating with the cyanide solution until the blue tint disappears. The copper ore is treated as in (i.), the copper being precipitated by aluminium, redissolved in nitric acid, and the resulting solution titrated in manner just described (*v.* Brearley, Chem. News, 1897 76, 189). (For other methods of separating and estimating copper, see also Zeitsch. anorg. Chem. 1896, ii. 268; Chem. Soc. Abstr. 1901, ii. 197; J. Amer. Chem. Soc. 1905, 27, 1224; Zeitsch. anal. Chem. 1907, 46, 128; J. Amer. Chem. Soc. 1908, 30, 760; Chem. Zeit. 1908, 33, 263; Amer. J. Sci. 1909, (iv.) 27, 448.)

(For electrolytic estimation of copper, *v.* ELECTRO-CHEMICAL ANALYSIS.)

Cadmium is separated from the other metals of Group II. by the methods indicated under *copper*, *lead*, &c. In the presence of zinc, Fox recommends precipitation in a solution containing trichloroacetic acid (Chem. Soc. Trans. 1907, 91, 964). Electrolytically, cadmium is deposited from a cyanide solution (0·7–1·2 amperes and 4·8–5 volts); the use of a rotating cathode accelerates the rate of deposition (compare

Flora, Amer. J. Sci. 1906, 70, 268 and 392; and Avery and Dales, J. Amer. Chem. Soc. 1897, 19, 379).

Tin, antimony, and *arsenic* are separated from the remaining metals of Group II. by digesting the group precipitate at 80° with concentrated yellow ammonium sulphide, when the sulphides of these three metals dissolve, leaving the other sulphides insoluble. Copper sulphide is appreciably soluble in this solvent, and in the presence of copper it is preferable to use sodium or potassium sulphide, but in the presence of mercury these reagents are inadmissible, owing to formation of the soluble double sulphide $Hg(SK)_2$. In the presence of much lead a small amount of tin is retained in the insoluble residue. Arsenic rarely occurs in alloys, and in these substances antimony and tin are separated from other metals as insoluble oxy-acids (metantimonic and metastannic acids) by the use of nitric acid as solvent.

Arsenic is separated from antimony and tin by distilling the hydrochloric acid solution of the three elements with ferrous chloride; the arsenic is volatilised as arsenious chloride; this compound is collected in cold water and the arsenic precipitated as trisulphide (Fischer, Zeitsch. anal. Chem. 1881, 21, 266). Various modifications of this method have been introduced; the distillation is carried on in a current of hydrogen chloride and hydrogen sulphide, the latter serving as the reducing agent instead of ferrous chloride; the volatilised arsenious chloride is converted in the cooled receiver into the trisulphide (Piloty and Stock, Ber. 1897, 30, 1649). (For other modifications, *see* Gooch and Danner, Amer. J. Sci. 1891, [3] 42, 308; Andrews, J. Amer. Chem. Soc. 1895, 17, 869; Rohmer, Ber. 1901, 34, 33; Morgan, Chem. Soc. Trans. 1904, 85, 1001.)

The arsenic may also be separated from tin and antimony by dissolving the three sulphides in ammoniacal hydrogen peroxide, neutralising the solution with mineral acid, acidifying with tartaric acid, and precipitating the arsenic as magnesium ammonium arsenate by the addition of ammonia and magnesia mixture (*see Qualitative analysis*).

The following method of separating arsenic and antimony in their ores, leads to volumetric processes for the determination of these elements (Low, J. Amer. Chem. Soc. 1906, 28, 1715). The mineral is decomposed by heating with strong sulphuric acid (20 parts) containing potassium hydrogen sulphate (1·4 parts), and 1 part of tartaric acid. The cooled product is taken up with 350 c.c. of hot water, 10 c.c. of strong hydrochloric acid, and 3 grams of tartaric acid, and the solution saturated with hydrogen sulphide. The mixed sulphides are dissolved in aqueous potassium sulphide, and the filtrate evaporated down with 10 c.c. of strong sulphuric acid and 3 grams of potassium hydrogen sulphate until the sulphur and the greater part of the free aid are expelled. The cooled melt is dissolved in 50 c.c. of strong hydrochloric acid and 25 c.c. of water, and arsenious sulphide precipitated by hydrogen sulphide. The antimony remaining in the filtrate is precipitated as sulphide by diluting the solution and passing in more hydrogen sulphide. The antimonious sulphide is again dissolved in potassium sulphide, the solution evaporated nearly to dryness with strong sulphuric acid and potassium hydrogen sulphate, the melt dissolved in dilute hydrochloric acid and titrated with standard permanganate.

The arsenious sulphide is dissolved in warm ammonium sulphide, and the solution heated strongly with strong sulphuric acid and potassium hydrogen sulphate until all the sulphur and nearly all the acid are expelled. The residue is boiled with water to expel sulphur dioxide, neutralised, and titrated with standard iodine solution in the presence of sodium bicarbonate.

Arsenic may also be estimated in minerals (which do not contain phosphates) by fusing the powdered ore with sodium carbonate and nitre or sodium peroxide, extracting the fused mass with water and precipitating silver arsenate from the neutralised solution. This precipitate is redissolved in nitric acid, and the amount of silver in it determined by standard thiocyanate; whence the quantity of arsenic present can be readily calculated. (For other processes for the estimation of arsenic in technically important materials, *v.* Clark, Chem. Soc. Trans. 1892, 61, 424; Friedheim, Zeitsch. anal. Chem. 1905, 44, 665; Heath, Zeitsch. anorg. Chem. 1908, 59, 87; Gooch and Phelps, Amer. J. Sci. 1906, (iv.) 22, 488; McGowan and Floris, J. Soc. Chem. Ind. 1905, 24, 265; Sanger and Black, *ibid.* 26, 1115; Collins, Analyst, 1912, 37, 229.) (For the detection and estimation of minute quantities of arsenic, *v.* ARSENIC.)

Separation of tin and antimony. In the absence of any large amount of lead or other metal giving a sulphide insoluble in ammonium sulphide, tin and antimony can be separated from these metals by means of this reagent, but if lead is present in considerable amount the tin is never completely extracted, a portion always remaining in the insoluble residue. In this case it is preferable to separate out the tin and antimony by oxidising them to their insoluble hydrated oxides by means of nitric acid. These oxides when fused with caustic soda in a silver crucible yield sodium stannate and antimonate; the latter of these salts is practically insoluble in dilute alcohol (1 vol. alcohol, 2 vols. water), whilst the former is readily dissolved. A repetition of this process with the insoluble antimonate leads to a complete separation.

When present as sulphides, these metals are conveniently dealt with by Henz's modification of Clark's method. The sulphides are dissolved in excess of aqueous caustic potash containing potassium tartrate; the solution is gradually heated to boiling with excess of 30 p.c. hydrogen peroxide. When the oxidation of the sulphides is complete, excess of oxalic acid is added (15 grams for 1 gram of mixed metal), the liquid boiled to destroy excess of hydrogen peroxide, and hydrogen sulphide passed for some time through the hot solution. The precipitated antimony sulphide is dealt with as described under gravimetric estimations. The filtrate is treated with sulphuric acid, concentrated to a small bulk (150 c.c.), and electrolysed at 60° with a current of 0·2–0·3 ampere, and 2·3 volts, using a rotating anode, when the deposition of the tin is complete in about one hour (Henz. Zeitsch. anorg. Chem. 1903, 37, 1; and Cahen and Morgan, Analyst, 1909, 34, 3).

In Clark's original process the filtrate from the antimony sulphide, which contains stannic tin, is mixed with yellow ammonium sulphide in excess and acidified with acetic acid. After some time the stannic sulphide is collected, washed with a solution of ammonium nitrate, and converted into stannic oxide by ignition. In accurate work the antimony sulphide is redissolved, and the oxalic acid separation repeated in order to obtain the last traces of tin (compare Carnot, Compt. rend, 1886, 103, 258). (For descriptions of other methods of estimating tin and antimony in their ores and alloys, see J. Soc. Chem. Ind. 1892, 11, 662; G. W. Thompson, J. Soc. Chem. Ind. 1896, 15, 179; T. Brown, jun., J. Amer. Chem. Soc. 1899, 21, 780; Argenot, Zeitsch. angew. Chem. 1904, 17, 1274; Lévy, Analyst, 1905, 30, 361; Panajotow, Ber. 1909, 42, 1296.)

The following process, due to Pearce, gives a rapid volumetric method for estimating tin in its ores. The mineral is fused in a nickel crucible with about 20 parts of sodium hydroxide with the addition of a little powdered charcoal; the fused mass is dissolved (excepting silica) in hydrochloric acid, and the solution reduced by the addition of iron rods or sheet nickel. The stannous chloride thus produced is titrated with standard iodine solution in presence of sufficient hydrochloric acid (1 : 4) to prevent the oxidation of any arsenic or antimony which may be present.

Gold and *platinum* are separated chiefly in the analytical subgroup containing arsenic, antimony, and tin. Fusion of the sulphides with sodium carbonate and nitre, followed by extraction with water, removes the arsenic. The residue, treated with zinc and hydrochloric acid, reduces tin and antimony to the metallic state; the former is dissolved by boiling hydrochloric acid, and the latter by nitric and tartaric acids, whilst gold and platinum are left. Treatment of the mixed metals with chlorine water removes gold, and dilute *aqua regia* then dissolves platinum, palladium, and rhodium. From this solution platinum is precipitated by ammonium chloride and alcohol, and from the filtrate, after neutralisation with sodium carbonate, palladium is precipitated as cyanide by mercuric cyanide.

For separation of palladium from gold, platinum, rhodium, and iridium by means of dimethylglyoxime, *see* Wunder and Thüringer, (Zeitsch. anal. Chem. 1913, 52, 660; Analyst, 1913, 524).

The residue from the *aqua regia* treatment is roasted in the air; osmium volatilises as the tetroxide, ruthenium sublimes as the dioxide, whilst iridium is left (*v.* Leidié, Compt. rend. 1900, 131, 888; and PLATINUM METALS).

Molybdenum is precipitated as sulphide preferably from a sulphuric acid solution by treatment with hydrogen sulphide under pressure. From the sulphides of the copper-lead subgroup, it is separated by digestion with sodium sulphide under pressure, when the molybdenum passes into solution and is reprecipitated as sulphide by dilute sulphuric acid. Molybdenum sulphide is separated from the sulphides of antimony and tin by dissolving the latter in hydrochloric acid. The sulphides of arsenic and molybdenum are dissolved in hydrochloric acid and potassium chlorate, the arsenic precipitated from the filtrate after adding ammonia and magnesia mixture as magnesium ammonium arsenate. The final filtrate is acidified, and the molybdenum reprecipitated as sulphide. Molybdenum is separated from phosphorus in a similar manner. From tungsten it is best separated by heating the mixed trioxides or their alkali salts at 250°–270° in a current of hydrogen chloride, when the molybdenum is completely volatilised as the additive compound $MoO_3,2HCl$, while the tungsten remains in the non-volatile residue (Debray, Compt. rend. 1858, 46, 1101: and Péchard, *ibid.* 1892, 114, 173).

Selenium and *tellurium* fall into the analytical sub-group containing arsenic, and after this element has been removed as magnesium ammonium arsenate (*v. Molybdenum*); the selenium and tellurium are precipitated by reducing agents such as sulphur dioxide, hydrazine, &c. (i.) Sulphur, selenium, and tellurium are separated by fusion with potassium cyanide in a stream of hydrogen. On dissolving the mass in water and passing air through the solution, the potassium telluride present is decomposed, and tellurium is precipitated. When the filtrate is acidified, the potassium selenocyanate (KCNSe) is decomposed, yielding selenium. (ii.) The mixed dioxides of selenium and tellurium are dissolved in aqueous caustic potash; the solution, faintly acidified with hydrochloric acid, is diluted to at least 200 c.c. with boiling water, rendered just ammoniacal and reacidified with acetic acid. After 30 minutes the tellurium dioxide is collected, washed with cold water, and gently ignited (Browning and Flint, Zeitsch. anorg. Chem. 1909, 64, 104).

Gold from all other metals: reduction of an acid solution by oxalic acid or sulphurous acid.

Selenium from the metals: reduction with sulphurous acid in hydrochloric acid solution.

GROUP III.—The metals of Group III*a.* are separated from those of the succeeding groups by precipitation with ammonia in presence of ammonium chloride; the metals of Group III*b.* are separated from those of the succeeding groups by means of ammonium sulphide (*v. General methods of estimation*).

Iron, aluminium, chromium, uranium, glucinum, and cerium, from zinc, manganese, nickel, cobalt. The solution, which must contain iron and uranium as ferric and uranic salts, is nearly neutralised, mixed with excess of finely divided and recently precipitated barium carbonate, and allowed to remain in a closed vessel at the ordinary temperature for some hours with occasional agitation. In presence of nickel and cobalt, ammonium chloride should be added to prevent precipitation of traces of these metals. Filter and wash with cold water. The precipitate may contain ferric, chromic, aluminium, glucinum, ceric and uranic hydroxides, mixed with barium carbonate; the filtrate contains the other metals, together with some barium. In both cases the barium can be removed by means of sulphuric acid, but as the barium sulphate carries down small amounts of the other metals, it is preferable to separate the metals of Groups III. and IV. by a double precipitation with ammonium sulphide (Treadwell).

Iron and aluminium from zinc, manganese, nickel, cobalt, uranium, and metals of the suc-

ceeding groups. The solution, which must contain iron as a ferric salt, is nearly neutralised by sodium or ammonium carbonate. In presence of iron the liquid becomes deep red, but no precipitate must be formed. Sodium, or, better, ammonium acetate, is added in sufficient but not excessive quantity, and the liquid is boiled until the precipitate becomes granular and settles rapidly. Prolonged boiling makes the precipitate slimy. The liquid is filtered whilst hot, and the precipitate is washed with hot water; if the liquid is allowed to cool the precipitate is partially redissolved. The precipitate is converted into ferric and aluminium oxides by ignition; the other metals are in the filtrate. It is advisable, and in presence of nickel essential, to redissolve the precipitate and repeat the process. This method is not available for the separation of chromium.

The same result can be obtained with ammonium formate or succinate.

Aluminium and chromium from iron, zinc, manganese, nickel, and cobalt. Mix the solution with a moderate quantity of pure normal potassium tartrate, then with pure caustic potash or soda until the precipitate redissolves, add ammonium sulphide in slight excess and allow to stand. Wash the precipitate with water containing ammonium sulphide. Aluminium and chromium are in the filtrate, the other metals in the precipitate. If iron and chromium are absent, it is sufficient to add the alkaline tartrate, excess of ammonia, ammonium chloride and ammonium sulphide.

Separation of iron and aluminium. The following methods have also been employed for this important separation. (i.) Potassium hydroxide dissolves aluminium hydroxide, but not ferric hydroxide; the former is reprecipitated from the filtrate by boiling with ammonium chloride or adding successively nitric acid and ammonia; the iron precipitate is dissolved in acid and reprecipitated by ammonia. (ii.) The two metals are precipitated with ammonia and the weight of the combined oxides determined. The mixture is then digested with strong hydrochloric acid (10 concentrated solution : 1 water) until all the iron has dissolved; the presence of free chlorine or hydriodic acid assists the solution of the ferric oxide. If alumina predominates, it may be necessary to fuse the mixed oxides with potassium pyrosulphate. The solution is saturated with hydrogen sulphide to reduce the iron to the ferrous condition; the excess of this sulphide is expelled by carbon dioxide, and the liquid titrated with standard permanganate. The proportion of aluminium is determined by difference. (iii.) Iron and aluminium may also be separated by treating the mixed chlorides with strong hydrochloric acid and ether (equal vols.); the aluminium chloride is precipitated, collected, washed with ethereal hydrochloric acid and ignited with mercuric oxide (Gooch and Havens, Amer. J. Sci. 1896, 2, 416). (iv.) The separation of small quantities of aluminium from excess of iron has been successfully effected by the use of phenylhydrazine. The iron is first reduced to the ferrous condition by adding hydrochloric acid and ammonium bisulphite, and the solution almost neutralised with ammonia, a slight excess of phenylhydrazine is then added, and after one hour the aluminium hydroxide is collected and washed with a solution of phenylhydrazine sulphite. In this way aluminium can be separated from iron, manganese, calcium, and magnesium (Hess and Campbell, J. Amer. Chem. Soc. 1899, 21, 776).

Separation of iron, aluminium, and phosphoric acid. When the total amount of these substances is small, the precipitate obtained by ammonia is ignited and weighed ($A = Fe_2O_3 + Al_2O_3 + P_2O_5$). The precipitate is then fused with sodium carbonate and silica, and the mass extracted with water containing a little ammonium carbonate. The residue containing iron and aluminium is evaporated down with sulphuric acid to dissolve the iron; the solution is reduced with hydrogen sulphide as in the preceding separation, and titrated with permanganate solution. The solution, which contains all the phosphoric acid, is evaporated down with hydrochloric acid to remove silica; the residue taken up with water, and the phosphoric acid precipitated from the filtrate as magnesium ammonium phosphate. From the weight of magnesium pyrophosphate obtained the amount of P_2O_5 is determined, and the Al_2O_3 is obtained by difference. If the total amount of these three substances is large, the original solution may be divided into three aliquot portions, in one of which the phosphoric acid is precipitated as ammonium phosphomolybdate, in the second part the iron is determined volumetrically, and from the third the total precipitate (Fe_2O_3, Al_2O_3, P_2O_5) is obtained (compare Cooksey, Analyst, 1908, 33, 437).

Chromium is readily separated from many metals, *e.g.* aluminium, by conversion into chromate, which is not precipitated by alkalis. This can be done in one of the following ways. (*a*) Make the solution alkaline with caustic potash or soda, saturate with chlorine, and then heat to expel excess of gas, and decompose hypochlorites by heating with ammonia. (*b*) Ammonium persulphate is added to a solution containing chromium, iron, and aluminium. On boiling, the chromium is oxidised to chromate, the acid set free during oxidation being sufficient to keep the iron and aluminium in solution (G. v. Knorre, Zeitsch. anorg. Chem. 1903, 16, 1097). (For the estimation of chromium in chromite and chrome steel, *see Volumetric section.*)

Aluminium from chromium. After chromium has been converted into chromic acid, the aluminium may be precipitated as hydroxide or as phosphate (*v. Determination of metals*). The filtrate is acidified, heated to boiling, and sodium thiosulphate added until the chromium is completely reduced; it can then be estimated as phosphate in the same way as aluminium; or caustic alkali is added to the solution of the metals until the precipitate at first formed redissolves. Bromine-water is added until the green colour of the solution is changed to the yellow of a chromate solution. The liquid is heated to boiling, and more bromine-water added drop by drop to precipitate the alumina in a non-gelatinous form.

Uranium is separated from the other metals of this group by the solubility of its hydroxide, sulphide, and acid uranates, in ammonium carbonate.

Uranium from Iron and Aluminium. An acid solution containing ammonium salts is mixed with excess of ammonium carbonate and ammonium sulphide in a closed flask. The precipitate contains ferrous sulphide and aluminium hydroxide; the uranium remains dissolved as the double carbonate $UO_2 \cdot CO_3,2(NH_4)_2CO_3$. The filtrate is concentrated considerably, acidified with hydrochloric acid, boiled, and the uranium precipitated as ammonium diuranate with ammonia. The precipitate is ignited and weighed as U_3O_8. Or this oxide is heated with dilute sulphuric acid (1 : 6) at 170 in an inert atmosphere (carbon dioxide): the solution which contains uranyl sulphate (2 mols.) and uranous sulphate (1 mol.), is titrated with standard permanganate solution.

$$1 \text{ c.c. } \frac{N}{10} KMnO_4 = 0 \cdot 03593 U.$$

Uranium ores are treated in the following way. The mineral (0·5–1·0 gram) is dissolved in nitric acid or *aqua regia*, silica removed by evaporation, the soluble residue extracted with hydrochloric acid, and the metals of the copper group precipitated by hydrogen sulphide. The filtrate is oxidised with potassium chlorate, and treated successively with ammonium phosphate, ammonia (till nearly neutral), and sodium carbonate in excess. The mixture is boiled and sufficient ammonium chloride added to decompose excess of sodium carbonate. The precipitate, which contains the iron, vanadium, &c., is washed with aqueous ammonium carbonate. This salt is removed from the filtrate by boiling alone and with nitric acid. The solution is almost neutralised with ammonia, and to the boiling liquid are added successively microcosmic salt, sodium thiosulphate, acetic acid, and finally ammonium acetate. The precipitate, uranyl ammonium phosphate, is collected, ignited, moistened with nitric acid, again ignited and weighed as $(UO_2)_2P_2O_7$.

Uranium is separated from thorium (and iron) by means of hydroxylamine hydrochloride, which in ammoniacal solution precipitates thorium and ferric hydroxides, leaving the uranium in solution (Jannasch and Schilling, Chem. Zeit. 1905, 29, 248).

Cerium is separated *from other metals* by saturating the solution with sodium sulphate, this salt being added in fine powder. A crystalline double sulphate of cerium and sodium separates, and is washed with a saturated solution of sodium sulphate.

Glucinum is precipitated with aluminium in Group III., and separated from aluminium and the other metals of the group by one of the following methods: (i.) A saturated solution of sodium hydrogen carbonate dissolves out glucinum hydroxide from a precipitate containing aluminium and ferric hydroxides, leaving the latter unaffected (Parsons and Barnes, J. Amer. Chem. Soc. 1906, 28, 1589). (ii.) Aluminium and glucinum chlorides are separated by saturating their solutions with hydrogen chloride in the presence of ether; the former is precipitated, the latter remaining dissolved (Amer. J. Sci. [4] 11, 416). (iii.) The acetates may be separated by the use of hot glacial acetic acid, from which solvent basic glucinum acetate $GlO_4(CO_2 \cdot CH_3)_3$ $[GlO_4(CH_3CO_2)_3]$ separates on cooling (Parsons and Robinson, *cf.* also Glassmann, Ber. 1906, 39, 3366; and J. Amer. Chem. Soc. 1895, 17, 688; Wunder and Wegner, Zeitsch. anal. Chem. 1912, 51, 470). This acetate is soluble in chloroform and may be distilled unchanged. Quantitative results may be obtained by volatilising the salt from the basic acetates of iron and aluminium (Kling and Gelin, Bull. Soc. chim. 1914, 15, 205; Analyst, 1914, 232).

Barium carbonate decomposes glucinum chloride, thus separating this metal from those of Group III*b*.

Vanadium is separated from the majority of metallic elements by fusion with sodium carbonate and potassium nitrate; the vanadium dissolves in water as sodium vanadate. Chromium and manganese would also be found in the aqueous extract, but from these metals vanadium is separated by the addition of ammonium sulphide in excess, when chromium and manganese are precipitated respectively as hydroxide and sulphide leaving vanadium in solution as a thiovanadate (cf. Zeitsch. anorg. Chem. 5, 381; Compt. rend. 1904, 138, 810; and Hillebrand, Amer. J. Sci. [4] 6, 209). From arsenic, vanadium may be separated either by reducing with sulphur dioxide and precipitating arsenious sulphide with hydrogen sulphide or by heating the mixed sulphides in hydrogen chloride at 150°, when the arsenic is volatilised (Field and Smith, J. Amer. Chem. Soc. 1896, 18, 1051).

Vanadium is separated from phosphoric acid by reducing vanadic acid to a hypovanadic salt with sulphur dioxide, and precipitating the phosphorus as phosphomolybdate.

Vanadium and molybdenum are separated by the action of hydrogen sulphide on vanadic and molybdic acids under pressure, molybdenum sulphide being precipitated, or ammonium metavanadate may be precipitated by the action of excess of ammonium chloride (Gibbs, Amer. Chem. J. 1883, 5, 371); the latter method serves to separate vanadium from tungsten.

(For methods of estimating vanadium in iron and steel, *see* Brearley and Ibbotson, The Analysis of Steel Works Materials; and Blair, The Chemical Analysis of Iron.)

Tungsten is separated from the majority of other elements by fusion with alkali carbonate and extraction of the alkali tungstate with water. This extract, when acidified with nitric acid and evaporated to dryness, yields tungstic acid as a residue insoluble in water. From arsenic and phosphoric acids tungstic acid is separated by the addition of magnesia mixture, which precipitates the arsenic and phosphorus, leaving the tungstate in solution (Gooch, Amer. Chem. J. 1871, 1, 412; and Gibbs, *ibid.* 1885, 7, 337).

The tungsten in wolframite may be estimated by fusing the finely powdered ore (0·5 gram) with 6 parts of fusion mixture in a platinum crucible for half an hour. The fused mass is extracted with boiling water when alkali tungstate passes into solution together with silicate and stannate. The insoluble residue contains iron, manganese, calcium, and magnesium with small amounts of columbic and tantalic acids. The filtrate is evaporated to dryness with excess of nitric acid, and the residue, after heating at 120°, is extracted with dilute ammonium nitrate solution; the residue, which consists of tungstic oxide with silica and stannic oxide, is weighed and then treated with hydrofluoric acid and weighed again. This second residue consists of tungstic oxide and stannic oxide, and the latter is volatilised by heating repeatedly with ammonium chloride until the weight of the final residue (WO_3) is constant.

To remove tin the mixed oxides may be ignited with zinc powder, and the residue, after extraction with hydrochloric acid, is tungsten trioxide (Angenot, Zeitsch. angew. Chem. 19, 140).

(For other separations of tungsten from its usual associates, *see* J. Amer. Chem. Soc. 1900, 22, 772; Zeitsch. anorg. Chem. 1905, 45, 396; Zeitsch. anal. Chem. 1908, 47, 37; Bull. Soc. chim. 1908, 13, 892; Wunder and Schapira, Ann. Chim. anal. 1913, 18, 257; Marbaker, J. Amer. Chem. Soc. 1915, 37, 86.)

Columbium and *tantalum* are extracted from columbite or tantalite by fusing the mineral with potassium hydrogen sulphate and extracting the fused mass with hot water and hydrochloric acid. The residue is treated with ammonium sulphide to remove tin, tungsten, and again extracted with hot hydrochloric acid. The final residue is then dissolved in hydrofluoric acid, the filtered solution is treated with potassium carbonate: potassium tantalofluoride separates in acicular crystals and the mother liquor furnishes potassium columbium oxyfluoride, crystallising in plates (compare Weiss and Landecker, Zeitsch. anorg. Chem. 1909, 64, 65; and Chesneau, Compt. rend. 1909, 149, 1132).

Titanium. In addition to the process given under the estimation of titanium, this element may be separated from iron by the following methods: (i.) By adding ammonium sulphide to an alkaline tartrate solution of the two elements, when ferrous sulphide is precipitated (Gooch, Amer. Chem. J. 1885, 7, 283). (ii.) By precipitating titanic acid with phenylhydrazine (J. Amer. Chem. Soc. 1895, 25, 421). Titanium is separated from aluminium by boiling with an alkali acetate and dilute acetic acid, when basic titanium acetate is precipitated.

Titanium and *zirconium* are separated by the following methods: (i.) A solution of the elements in dilute sulphuric and acetic acids is boiled for some time, when titanic acid is precipitated (J. pr. Chem. 1869, 108, 75; Zeitsch. anal. Chem. 9, 388). (ii.) The acid solution is boiled with zinc till the titanium is reduced to titanous salt, the zirconium is then precipitated by the addition of potassium sulphate (Compt. rend. 1863, 57, 298). (iii.) A neutral solution of the nitrates is added drop by drop to a boiling concentrated solution of ammonium salicylate ($1 : 5H_2O$), the solution boiled for one hour, concentrated, and the precipitated zirconium salicylate collected and washed with ammonium salicylate solution. Titanium salicylate is soluble in hot water and remains in the filtrate (Dittrich and Freund, Zeitsch. anorg. Chem. 1907, 56, 337, 348).

Cerium is precipitated in the aluminium group (III.*a*), and, together with the other metals of the rare earths, is separated from iron and aluminium by means of oxalic acid or ammonium oxalate. From lanthanum, praseodymium, and neodymium it may be separated by suspending the hydroxides in aqueous caustic potash and passing in chlorine until the liquid is no longer alkaline. The cerium remains precipitated as the yellow hydrated dioxide, whilst the other hydroxides are dissolved (Mosander). Various methods have been proposed similarly based on the oxidation of cerous compounds to the ceric condition (*v.* Ann. Chem. Pharm. 131, 359; Monatsh. 1884, 5, 508; Ber. 35, 672).

Thorium, together with the rare earths, is separated from the other elements by oxalic acid. The further separation is effected by the following methods:—

(i.) Monazite sand is heated with concentrated sulphuric acid at 180°–200° for 2 to 3 hours, and the product taken up with water, and the rare earths precipitated by the addition of oxalic acid. The precipitated oxalates, after washing till free from phosphoric acid, are ignited, and the resulting oxides dissolved in hydrochloric acid. The excess of acid is expelled by evaporation at 100°, the residue dissolved in water and treated with sodium thiosulphate. After 12 hours the solution is boiled for 10 minutes and filtered. The precipitate contains thorium, but contaminated with cerium; it is therefore redissolved and the precipitation repeated until the filtrate gives no precipitate on boiling with ammonia. At this stage the precipitate is ignited, fused with sodium hydrogen sulphate, the product dissolved in water, and the thorium finally precipitated with oxalic acid, the precipitate being ignited and weighed as ThO_2 (Fresenius and Hintz, Zeitsch. anal. Chem. 35, 543).

(ii.) The mixed oxalates obtained as before from the monazite sand are decomposed, and the metals converted into nitrates by repeated evaporation with nitric acid. The neutral solution of the nitrates is diluted with aqueous ammonium nitrate (10 p.c.) warmed to 80°, and the thorium precipitated as peroxide by the addition of pure hydrogen peroxide solution. The precipitate, which contains a trace of cerium peroxide, is filtered, washed with aqueous ammonium nitrate, ignited and weighed as ThO_2 (Benz, Zeitsch. angew. Chem. 1902, 15, 297; compare Chem. Zeit. 1908, 32, 509).

(iii.) Precipitation by organic acids. (*a*) Fumaric acid precipitates thorium fumarate in 40 p.c. alcohol, leaving the other rare earths in solution (Metzger, J. Amer. Chem. Soc. 1902, 24, 901). (β) *m*-Nitrobenzoic acid in aqueous solution precipitates its thorium salt, the separation being complete in the presence of aniline. Under these conditions, cerium, praseodymium, neodymium, and lanthanum remain in solution (Kolb and Akele, Zeitsch. angew. Chem. 1905, 18, 92).

(iv.) Boiling with potassium azide in neutral solution leads to the precipitation of thorium hydroxide, the salts of the other rare earth metals being unaffected (Dennis, J. Amer. Chem. Soc. 1896, 18, 947). Fusion with potassium hydrogen fluoride separates thorium and cerium from zirconium, for on extraction with water containing a little hydrogen fluoride, potassium zirconofluoride dissolves, leaving behind the fluorides of thorium and cerium (Chem. News, 1897, 75, 230).

Manganese and *iron* are separated in their alloys (ferromanganese, &c.) by dissolving the alloy in hydrochloric acid with a little nitric acid. After boiling off nitrous fumes, the solution is filtered and diluted with boiling water to 600 c.c. Ammonia is added till a faint turbidity remains, excess of neutral ammonium acetate is then quickly added, and the solution boiled. The basic ferric acetate thus precipitated contains some manganese; it is therefore redissolved and the separation repeated. The united filtrates are treated with excess of bromine followed by strong ammonia also in excess; the liquid is vigorously agitated during the addition of these reagents, and then heated slowly to boiling. The precipitate is collected, washed with boiling water, ignited and weighed as Mn_3O_4 (compare Riggs, Amer. J. Sci. 43, 135; Gooch, Zeitsch. anorg. Chem. 1898, 17, 268; Brearley and Ibbotson, Chem. News, 1902, 82, 209; Zeitsch. anal. Chem. 1904, 43, 382; Jannasch and Rühl, J. pr. Chem. 1905, 72, 1; Moore and Miller, J. Amer. Chem. Soc. 1908, 30, 593).

Nickel from cobalt. The solution, which should contain but little free acid, is mixed with excess of pure potassium cyanide free from cyanate (the ordinary cyanide is fused with charcoal, dissolved in water, filtered, and evaporated in a silver dish), heated to boiling, and mixed with a solution of mercuric oxide in mercuric cyanide. The precipitate, when washed, dried, and ignited, leaves a residue of nickel oxide NiO, which is weighed. Cobalt is usually determined by difference; but if direct estimation is required, the filtrate from the nickel is evaporated to dryness, heated for some time with strong sulphuric acid, and the cobalt estimated in the solution.

Nickel can be separated from cobalt and all the other metals of Groups III. and IV. by precipitation in ammoniacal or dilute acetic acid solution with dimethylglyoxime (*see Estimation of nickel*). If ferric salts are present, they should be reduced to the ferrous condition, or tartaric acid is added before rendering the solution alkaline; the organic acid prevents the co-precipitation of iron, chromium, and aluminium (Brunck, Zeitsch. angew. Chem. 1907, 20, 1845).

Cobalt from nickel. (i.) In acetic acid solution, nitroso-β-naphthol precipitates the cobalt as cobaltic nitroso-β-naphthoxide (Ilinski and Knorre, Ber. 18, 699). (ii.) Cobaltic hydroxide is precipitated from a neutral solution of the two metals by barium carbonate and bromine water (Taylor, Proc. Manchester Phil. Soc. 1902, 46, (ii.) 1). (iii.) Small quantities of cobalt can be detected and estimated in the presence of nickel by adding to a neutral solution concentrated aqueous ammonium thiocyanate. On shaking with amyl alcohol and ether, these organic solvents extract the double salt $(NH_4)_2Co(CNS)_4$ (blue solution), leaving the nickel in the aqueous solution (Ber. 1901, 34, 2050 and 3913). Zinc is also removed with the cobalt.

Cobalt is precipitated as double nitrite on adding potassium nitrite to an acetic acid solution of the two metals; the nickel is left in solution (Fischer, Pogg. Ann. 72, 477; and Funk, Zeitsch. anal. Chem. 1907, 46, 1).

The solution is treated with ammonium chloride, ammonia, and hydrogen peroxide, and warmed, when $[Co(NH_3)_5Cl]Cl_2$ is formed. On neutralising by means of acid, cooling, and adding excess of ammonium molybdate, the cobalt is precipitated as $Co_2O_3,10NH_3,6MoO_3$. This is washed with water and dried at 110° (Carnot, Bull. Soc. chim. 1917 [iv.] 21, 211).

Separation of zinc, manganese, nickel, and cobalt. The slightly acid solution of the four metals is treated with sodium carbonate till a permanent precipitate is formed, which is redissolved by a few drops of hydrochloric acid; then for every 100 c.c. of liquid 15 drops of the same acid are added, followed by 10 c.c. of 20 p.c. ammonium thiocyanate; the solution heated to 70° is then saturated with hydrogen sulphide; the zinc in the precipitate is determined either as sulphide or oxide. Manganese is separated from nickel and cobalt by passing hydrogen sulphide into a solution of their salts in acetic acid containing excess of ammonium acetate, when nickel and cobalt are precipitated as sulphides; the filtrate may, however, still contain small amounts of these metals. The solution is concentrated, treated with ammonium sulphide, and then with acetic acid. A further precipitate of nickel and cobalt sulphides is thus obtained (*v.* Treadwell and Kramers, Zeitsch. anorg. Chem. 1901, 26, 184; compare J. Soc. Chem. Ind. 1905, 24, 228; Bull. Soc. Chim. 1908, (iv.) 3, 114).

Zinc from nickel and cobalt. Add excess of pure potassium cyanide and precipitate the zinc with sodium sulphide.

GROUP IV.—The metals of this group are separated from those of the following group by precipitation with ammonium carbonate (*v. General methods of estimation*). The liquid is first made alkaline with ammonia and afterwards heated to boiling to ensure complete precipitation.

Barium from calcium and strontium. The dilute neutral or feebly acid solution is mixed with excess of freshly prepared hydrofluosilicic acid and one-third its volume of 95 p.c. alcohol allowed to stand twelve hours, collected on a weighed filter, washed with a mixture of equal parts of water and alcohol, and dried at 100°. Calcium and strontium are not precipitated.

Barium from strontium. Ammonium bichromate and ammonium acetate are added alternately to a solution of barium and strontium salts containing ammonium acetate. After three hours the precipitate, $BaCrO_4$, is washed with ammonium acetate solution, dried at 180°, and weighed (Kahan, Analyst, 1908, 33, 12; *v.* Zeitsch. anal. Chem. 1905, 44, 742; J. Amer. Chem. Soc. 1908, 30, 1827).

Barium and strontium from calcium. The solution is mixed with a concentrated solution of ammonium sulphate, using 50 parts of the latter salt for one part of the mixed salts, heated to boiling with addition of a small quantity of ammonia, and the precipitate washed with water containing ammonium sulphate. The filtrate contains the calcium, which can be precipitated by ammonium oxalate.

Calcium from strontium. Convert the metals into nitrates, evaporate to dryness, and extract with a mixture of equal volumes of alcohol and ether, which dissolves calcium nitrate but not strontium nitrate.

Calcium from strontium and barium. The nitrates are dried at 140° and extracted with amyl alcohol, which dissolves out the calcium salt, leaving the other two undissolved (Browning, Amer. J. Sci. 43, 50, 314).

Calcium from magnesium. The calcium is precipitated by ammonium oxalate (*v. Determination of metals*), adding sufficient of this salt to convert both metals into oxalates, since calcium oxalate is appreciably soluble in a solution of magnesium chloride. In very accurate separations the precipitate should be filtered off, redissolved in hydrochloric acid, and reprecipitated by adding excess of ammonia and a small quantity of ammonium oxalate (*cf.* Richards, Zeitsch. anorg. Chem. 1901, 28, 71; Zeitsch. angew. Chem. 1908, 21, 592; J. Amer. Chem. Soc. 1909, 31, 917).

GROUP V.—*Magnesium from alkalis.* The magnesium is precipitated with ammonium phosphate in the usual way, the filtrate evaporated to dryness, heated to expel ammonium salts, the residue evaporated two or three times with strong nitric acid to remove hydrochloric acid, and the phosphoric acid removed by stannic oxide (*v. Phosphoric acid from metals*; *v.* Gibbs, Amer. J. Sci. [3] 5, 114; Neubauer, Zeitsch. angew. Chem. 1896, 9, 439; Gooch, Zeitsch. anorg. Chem. 1899, 20, 121).

In solutions free from ammonium salts, the magnesium can be precipitated as magnesium hydroxide by the addition of aqueous barium hydroxide. The excess of barium is removed by ammonium carbonate and the alkalis are determined in the filtrate. Magnesium chloride is also separated from the alkali chlorides by ignition with mercuric oxide, when mercuric chloride and the excess of oxide volatilise, leaving magnesia, from which the soluble alkali chlorides are readily separated.

Alkalis from magnesium. (*a*) The solution is made distinctly alkaline with pure milk of lime (calcium hydroxide suspended in water) and boiled for some time, care being taken that it remains alkaline. The liquid is filtered, made alkaline with ammonia, and the calcium precipitated by adding ammonium carbonate and a small quantity of ammonium oxalate. The filtrate is acidified with hydrochloric acid and evaporated in a weighed platinum dish, heated to expel ammonium salts, and the alkaline chlorides weighed. They should dissolve completely in water and should give no precipitate when mixed with ammonium carbonate and allowed to stand for some time. If any calcium is present, it must be removed by repeating the treatment with ammonium carbonate and oxalate.

(*b*) The solution, which must contain only potassium, sodium, and magnesium, is mixed with excess of oxalic acid, evaporated to dryness, and the oxalic acid expelled by heating carefully over a lamp until white fumes cease to come off. The residue is treated with water, when potassium and sodium dissolve as carbonates, whilst magnesium oxide remains undissolved.

Alkalis from silicates. (*a*) The finely powdered silicate (1 gram) is mixed intimately with an equal weight of ammonium chloride and eight parts of dense granular calcium carbonate, and heated to redness for half an hour. The product is boiled with water in a platinum or silver dish for two hours, care being taken to make up the loss by evaporation, the liquid is filtered and the residue well washed with hot water. The filtrate, which contains calcium and the alkalis, is treated in the manner just described. In this method of decomposition, which is due to J. Lawrence Smith, the silicate is decomposed by the calcium oxide, which is dissolved by the fused calcium chloride formed by the action of the ammonium chloride on the calcium carbonate.

(*b*) The silicate is treated in a platinum dish with excess of sulphuric and hydrofluoric acids, and the mixture evaporated on the water-bath until the mineral is entirely decomposed. The temperature is then raised to drive off the greater part of the sulphuric acid, and the cooled residue extracted with water. The sulphates are converted into chlorides by barium chloride, the metals of Groups III. and IV. precipitated by ammonia and ammonium carbonate, the magnesium removed by barium hydroxide, and the excess of this reagent eliminated by ammonia and ammonium carbonate. The alkali chlorides remaining in the final filtrate are estimated as indicated in the following section. Certain native silicates of the andalusite group are not decomposed completely by this treatment with hydrofluoric acid; these minerals may, however, be broken up by ignition with ammonium fluoride.

(*c*) The alkali and other metals contained in a refractory silicate may be separated by heating the mineral with lead carbonate. The product is extracted with nitric acid; the lead removed as chloride and sulphide, and the metals in solution dealt with in the customary manner (Jannasch, Zeitsch. anorg. Chem. 1895, 8, 364).

(*d*) Silicates of different types are decomposed by fusion with boric anhydride followed by extraction with methyl alcoholic hydrogen chloride and evaporation to remove the boric acid as volatile methyl borate (Ber. 1895, 28, 2822; Zeitsch. anorg. Chem. 1896, 12, 208).

Potassium from sodium. The metals are converted into chlorides, which are evaporated to dryness and weighed together after drying at 150°. The salts are dissolved in water, mixed with platinic chloride in sufficient quantity to convert both into platinichlorides, and evaporated nearly but not quite to dryness. The residue is then treated with alcohol, which dissolves the sodium but not the potassium salt (*v. Potassium*). If the mixture is evaporated to complete dryness and heated so that the sodium platinichloride becomes anhydrous, it dissolves with difficulty in alcohol. Under some conditions reversion takes place and sodium chloride separates in white crystals insoluble in alcohol. In this case the alcohol is very carefully evaporated and the residue again treated with platinic chloride.

In order to separate small quantities of potassium from large quantities of sodium, advantage may be taken of the fact that potassium chloride is more soluble than sodium chloride in strong hydrochloric acid (Zeitsch. analyt. Chem. 1880, 156). The dry mixed chlorides are thoroughly moistened with concentrated hydrochloric acid: 2 c.c. of the acid is then added, and the salt thoroughly crushed and stirred with a glass rod. After standing for a few minutes the acid is poured off into a small dish. Ten repetitions of this treatment, using 2 c.c. of acid each time, will suffice to remove all potassium, whilst the greater part of the sodium chloride is not dissolved. The acid solution is evaporated to dryness and the potassium determined as platinichloride (Chem. Soc. Trans. 39, 506). By adopting this plan much less platinic chloride is required, and the separation is much more accurate.

Lithium from sodium and potassium When a lithia-containing silicate (*e.g.* lepidolite) is broken up by one of the preceding processes the precipitable metals of Groups I.–IV. are first removed and the alkali metals converted into chlorides. The combined chlorides are dried and weighed; potassium is estimated in one portion, and in a second portion the lithium is estimated by extracting the chlorides with amyl alcohol, or better, *iso*butyl alcohol, or with ether-alcohol saturated with hydrogen chloride. Anhydrous lithium chloride is soluble in these media, whereas sodium and potassium chlorides are practically insoluble therein (*cf.* Winkler, Zeitsch. anal. Chem. 1913, 52, 628; Analyst, 1913, 581; Palkin, J. Amer. Chem. Soc. 1916, 38, 2326; Analyst, 1917, 54). Lithium chloride has also been separated from the chlorides of the other alkali metals and barium by dissolving it in boiling pyridine, in which the others are insoluble (Kahlenberg and Krauskopf, J. Amer. Chem. Soc. 1908, 30, 1104; Skinner and Collins, J. Soc. Chem. Ind. 1913, 32, 214). (For the separation of lithium as phosphate and fluoride, *see* Ann. Chim. Phys. 98, 193; Frdl. 29, 332, and Analyst, 16, 209.)

Rubidium and *cæsium* are separated from each other and from potassium by taking advantage of the difference in the solubility of their platinichlorides. Rubidium hydrogen tartrate is more than nine times less soluble than the cæsium salt. Cæsium carbonate alone of the alkali carbonates is soluble in alcohol. Cæsium gives rise to a series of sparingly soluble perhalides and yields double chlorides with lead and antimony chlorides (*v.* Wells, Amer. J. Sci. 43, [3] 17; and Amer. Chem. J. 1901, 26, 265). The metals may also be separated by taking advantage of the different solubilities of their respective alums, particularly of their iron alums (Browning and Spencer, Amer. J. Sci. 1916, 42, 279).

Ammonium salts can be removed from a solution in two ways: (1) By evaporating to dryness and carefully heating over a lamp until all fumes cease to come off. (2) By concentrating the solution and heating for some time with excess of strong nitric acid. When evolution of oxides of nitrogen ceases, the liquid is evaporated to complete dryness and the nitrates converted into chlorides by repeated treatment with hydrochloric acid if necessary.

B. *The Estimation of Acid Radicals.*

Bromine from chlorine. (*a*) The two elements are precipitated by excess of silver nitrate and weighed together. The filter ash is removed, the precipitate cautiously heated to fusion, and a portion poured into a weighed porcelain boat. The boat is again weighed, heated to fusion in a current of dry chlorine in a glass tube until all bromine is expelled, and the silver chloride formed is weighed. It is advisable to heat in chlorine for a further period of ten minutes and weigh again. The loss of weight multiplied by 4·223 gives the amount of silver bromide in the weight of precipitate treated with chlorine, from which the quantity in the whole precipitate is readily calculated (*v. Indirect methods of determination*).

This method gives accurate results if the proportion of bromine is not too small. When a small quantity of bromine is mixed with a large quantity of chlorine, the former may be concentrated by taking advantage of the fact that if a limited quantity of silver nitrate is added, the precipitate will contain all the bromine, but only a portion of the chlorine. In one portion of the substance the two elements are determined together by complete precipitation. Another portion in somewhat dilute solution is mixed with a quantity of silver nitrate insufficient for complete precipitation, and allowed to stand in the cold for some time with repeated agitation. The precipitate is collected, washed, and weighed, and the proportion of bromine determined in the manner already described. The quantity of silver nitrate which should be used depends upon the relative proportions of chlorine and bromine. If one part of bromine is present for every 1000 parts of chlorine, one-fifth or one-sixth of the silver necessary for complete precipitation should be used; if one part to 10,000, only one-tenth; if one part to 100,000, only one-sixtieth (Fehling).

(*b*) The solution of the two halides heated at 70°–80° is treated with ammonium persulphate, and the liberated bromine volatilised in a current of air, collected in sulphurous acid, and estimated as silver bromide (Engel, Compt. rend. 1894, 118, 1263).

Iodine is separated from chlorine in exactly the same way as bromine from chlorine. The loss of weight on treating with chlorine, multiplied by 2·569, gives the weight of silver iodide in the portion of precipitate taken.

Iodine from chlorine or bromine. The solution is slightly acidified with hydrochloric acid, mixed with palladious chloride until precipitation is complete, and allowed to stand in a warm place for twenty-four or forty-eight hours. The precipitate of palladious iodide PdI_2 is collected on a weighed filter, washed with warm water, and dried at 100°, or is reduced by heating in hydrogen and the metal weighed.

Iodine can also be liberated by nitrous acid and estimated volumetrically (*v. Volumetric methods*).

Bromine, chlorine, and iodine from one another. (*a*) The three elements are precipitated and weighed together in one part of the solution. In another part the iodine is separated as palladious iodide by palladious chloride, or better, nitrate; the excess of palladium is removed by hydrogen sulphide and excess of the latter by ferric sulphate; and the chlorine and bromine in the filtrate are precipitated completely or fractionally and the bromine determined in the manner previously described. The chlorine is estimated by difference.

(*b*) A direct method of estimating the three halogens in a mixture of their soluble salts has been investigated by Jannasch and his collaborators. The process in its present stage of development gives a sharp separation of chlorine and iodine, but the results for bromine are rather low. The mixture dissolved in 25 c.c. of water is heated to boiling with acetic acid and hydrogen peroxide, and the liberated iodine expelled by a current of carbon dioxide. The bromine is then liberated by adding excess of hydrogen peroxide and moderately strong sulphuric acid (5 : 3). The iodine is collected in an ammoniacal solution of hydrazine sulphate and the bromine in alkaline hydrazine sulphate. After acidifying with nitric acid, the iodine and bromine are precipitated as silver salts, and the chlorine left in the distilling flask is similarly precipitated (Ber. 1906, 39, 196, 3655; J. pr. Chem. 1908, 78, 29; Zeitsch. anorg. Chem. 1, 144 and 245). (For other processes for separating the halogens, *see Volumetric section*; and Monatsh. 13, 1; Chem. Soc. Trans. 1893, 63, 1051; Compt. rend. 1898, 126, 187; Ber. 1899, 32, 3615.)

Several indirect methods of estimating these three elements in a mixture have been proposed. They are based on the methods given, together with the fact that the radicals may be precipitated exactly by a standard solution of silver nitrate and the precipitate weighed, the proportion of silver and halides in the precipitate being thus determined (*v.* Fresenius, Quantitative Analysis, sect. 5).

Indirect Methods of Determination. This estimation of two or three halogens in a mixture furnishes a good example of indirect methods of analysis, which are adopted in those cases where the separation of two or more constituents is either impossible or inconvenient. The calculation of the relative proportions of these constituents becomes possible when one can obtain as many independent relationships as there are radicals to be determined. The estimation of chlorine and bromine (*a*) is a case in point. The loss of weight due to the replacement of Br.(79·92) by Cl(35·46) is proportional to the amount of bromine present. Let w = loss of weight. Now

$$\frac{Cl}{Br} = \frac{35{\cdot}46}{79{\cdot}92} \text{ and hence } Br - \frac{35{\cdot}46}{79{\cdot}92}Br = w;$$

or Br = 1·797 w: *i.e.* the loss of weight multiplied by 1·797 gives the quantity of bromine present.

Similarly, the halogens in a mixture of soluble chloride, bromide, and iodide can be calculated from the following data: (i.) the amount of iodine present, set free by nitrous acid or hydrogen peroxide and acetic acid; (ii.) the total weight of mixed silver halides obtained from a known amount of mixture; (iii.) the silver required for the complete precipitation of the three halogens; this is obtained volumetrically. The indirect method can also be applied to the estimation of sodium and potassium contained in the mixed chlorides from a silicate analysis (*v. supra*). The data required are: (i.) the weight A of mixed chlorides; (ii.) the weight B of chlorine therein contained, this amount being determined either gravimetrically or volumetrically. Let x and y be the amounts of potassium and sodium respectively, then these quantities are readily calculated from the following equations, where Cl, K, and Na represent the atomic weights of these elements.

$$x + y = A - B$$

$$\frac{Cl}{K}x + \frac{Cl}{Na}y = B$$

These indirect methods give useful results only when the atomic or molecular weights of the two radicals differ considerably, and when the quantities present are approximately equal. Moreover, the results are affected to a considerable extent by comparatively small experimental errors.

Cyanide from chloride. Silver nitrate is added in excess to an approximately 2 p.c. solution of soluble cyanide and chloride. An excess of normal nitric acid is now added, and the mixture containing the freshly precipitated silver salts is distilled, when hydrocyanic acid is expelled quantitatively and estimated in the distillate by precipitation as silver cyanide with acidified silver nitrate, drying this precipitate at 110°, and weighing in a Gooch crucible or on a tared filter paper (Plimmer, Chem. Soc. Trans. 1904, 85, 12; compare also Richards and Singer, Amer. Chem. J. 1902, 27, 205).

Phosphoric acid from metals. (*a*) The nitric acid solution, as free as possible from hydrochloric acid, and free from silicic and arsenic acids, is mixed with excess of a solution of ammonium molybdate in nitric acid, heated gently for a few minutes, and filtered after standing for a short time. The precipitate is washed with dilute nitric acid, dissolved in ammonia, and the phosphoric acid precipitated by magnesia mixture. This method is more especially applicable when the quantity of phosphoric acid is relatively small. To prepare ammonium molybdate solution, 25 grams of the salt is dissolved in 100 c.c. of dilute ammonia, and the solution poured gradually with constant and vigorous agitation into 500 c.c. of a mixture of 3 vols. strong nitric acid and 1 vol. water. The liquid is heated at 50° for some time and the clear solution drawn off.

(*b*) By stannic oxide. The nitric acid solution is concentrated, mixed with fuming nitric acid boiling at 86°, heated gently, and granulated tin added gradually in quantity not less than four times the amount of phosphoric acid present. The stannic oxide produced forms an insoluble compound with the phosphoric acid. This is filtered off, washed with hot water, dissolved in caustic potash, the solution saturated with hydrogen sulphide, acidified with acetic acid, and the stannic sulphide removed. The filtrate is concentrated, any stannic sulphide which separates subsequently is removed, and the phosphoric acid is estimated in the usual way. The original filtrate from the stannic oxide contains the metals previously combined with the phosphoric acid.

(*c*) The nearly neutral solution is mixed with silver nitrate and digested for some time with excess of silver carbonate. The phosphoric acid separates as silver phosphate, the metals remain in solution with the excess of silver nitrate. The silver is removed by hydrochloric acid.

(*d*) When the phosphoric acid is combined with metals which form phosphates insoluble in water but soluble in acetic acid, the solution is nearly neutralised, mixed with sodium or ammonium acetate, and a slight excess of ferric chloride containing a known weight of iron added. The liquid is heated to boiling, the mixture of ferric phosphate and basic acetate washed with hot water, dried, and heated in a platinum crucible until the weight is constant. The weight of the precipitate *minus* the known weight of the ferric oxide gives the phosphoric anhydride P_2O_5. The precipitate may be moistened with nitric acid before the final ignition.

Phosphoric acid in silicates. In the analysis of silicates (*v. supra*) the phosphoric acid is found together with iron and aluminium in the precipitate produced by ammonia in the filtrate from the silica. This mixture is analysed in accordance with the method indicated under the separations of metals (Group III.).

Phosphorus and silicon in iron and steel. The iron or steel borings are dissolved in nitric acid ($1HNO_3$ sp.gr. 1·4 : $1H_2O$); the solution evaporated to dryness, and the residue ignited carefully until all the ferric nitrate is converted into ferric oxide. The ignited residue is dissolved in concentrated hydrochloric acid heated nearly to boiling, when the ferric oxide and phosphate pass into solution, leaving insoluble silica. The solution is evaporated to dryness, moistened with strong hydrochloric acid, and taken up with water; the silica is collected, ignited, and weighed, its purity being tested by treatment with hydrofluoric and sulphuric acids. The phosphoric acid in the filtrate is estimated by either of the following methods.

(*a*) The ferric solution, diluted and almost neutralised with ammonia, is reduced with sulphurous acid or sodium sulphite. Hydrochloric acid is added and the excess of sulphur dioxide expelled by boiling. A small portion of the ferrous iron is now reoxidised with a few drops of bromine water. Ammonia is added carefully till a brown precipitate is formed which becomes green on stirring. Acetic acid is added till the precipitate either dissolves or becomes whiter, and the solution then heated to boiling. The precipitate, which contains all the phosphorus as ferric phosphate mixed with basic ferric acetate, is dissolved in hydrochloric acid, the solution evaporated nearly to dryness, excess of citric acid added, and then magnesia mixture and ammonia. The magnesium ammonium phosphate is redissolved in hydrochloric acid and reprecipitated in the presence of citric acid to remove a small amount of iron, and ignited and weighed as $Mg_2P_2O_7$.

(*b*) The filtrate from the silica is evaporated to dryness, the residue dissolved in dilute nitric acid, ammonium nitrate added, and the solution heating to boiling. A boiling solution of ammonium molybdate is then added to phosphate solution, when ammonium phosphomolybdate is precipitated quantitatively. This precipitate is redissolved in ammonia to which ammonium nitrate and ammonium molybdate are added, and reprecipitated by adding hot nitric acid to the boiling solution. The compound is now pure, and is collected, washed with water containing ammonium nitrate and nitric acid, and either dried at 160°–180° or gently ignited. In the former case it is weighed as $(NH_4)_3PO_4,12MoO_3$ (containing 3·782 p.c. P_2O_5) or in the latter as $P_2O_5,24MoO_3$ (containing 3·946 p.c. P_2O_5) (*v.* Ber. 1878, 11, 1640; Zeitsch. anorg. Chem. 1893, 32, 144; Amer. Chem. J. 34, 204; Analyst, 1909, 34, 392; Chem. Zeit. 21, 442).

Separation of phosphoric and titanic acids (*v.* J. Soc. Chem. Ind. 1895, 14, 443). Estimation of phosphorus in phosphor-bronze (*v.* J. Amer. Chem. Soc. 1897, 19, 396) in phosphor-tin (J. Soc. Chem. Ind. 1908, 27, 427).

Silicic acid from titanic acid. The silica and titanium dioxide are weighed together, the mixture fused with a somewhat large quantity of potassium hydrogen sulphate, and the cooled mass extracted with water. Silica is left undissolved, titanic oxide dissolves, and can be precipitated from the filtrate by ebullition (*v. Titanium*).

Sulphides. If the sulphides are decomposable by hydrochloric acid, the hydrogen sulphide is absorbed in hydrochloric acid containing bromine (*v. Determination of metals*). Insoluble sulphides are decomposed by gently heating with *aqua regia* or with hydrochloric acid and bromine, and the sulphuric acid estimated in the solution. The latter method gives the total sulphur.

Sulphur in coal and coke. The finely powdered material (1 gram) is mixed intimately with 1 gram of calcined magnesia and 0·5 gram of sodium carbonate, and ignited to dull redness in an open platinum crucible for 1 hour, the mixture being stirred every five minutes with a platinum wire. The mixture is then heated strongly for 10 minutes with 1 gram of ammonium nitrate. The residue is extracted with water and the sulphate determined in the usual way (Eschka). The sulphur may also be determined by heating the coal with sodium or potassium carbonate (4 parts) alone, and extracting the residue with hydrochloric acid and a few drops of bromine (Nakamura). (*Compare* also Zeitsch. angew Chem. 1905, 18, 1560; Chem. Zeit. 1908, 32, 349; J. Russ. Chem. Soc. 1902, 34, 457.)

Sulphur in pyrites. The pyrites is oxidised either by fusion with sodium peroxide and sodium carbonate or by oxidation with nitric acid and bromine. These processes convert the sulphur to sulphate, which is estimated in the usual way (*v.* J. pr. Chem. 1892, [2] 45, 103; Zeitsch. anorg. Chem. 6, 303; *l.c.* 1896, 12, 129; J. Soc. Chem. Ind. 1905, 24, 7; Chem. News, 1906, 93, 213).

A convenient method of determining sulphur in pyrites consists in oxidation with bromine in carbon tetrachloride solution, followed by treatment with nitric acid, and precipitation of the sulphuric acid as barium sulphate after removal of silica and reduction of ferric salts (J. Soc. Chem. Ind. 1912, 919). Bartsch (Chem. Zeit. 1919, 43, 33) finds that the sulphur in pyrites yields hydrogen sulphide when treated with hydrobromic acid in contact with mercury and bases on this observation a rapid method for the valuation of pyrites. For details of the process and the apparatus employed, *see* Analyst, 1919, 148.

Sulphuric acid from all other acids except hydrofluosilicic by precipitation with barium chloride in presence of hydrochloric acid.

Sulphuric acid from hydrofluosilicic acid. The solution is mixed with excess of potassium chloride and an equal volume of strong alcohol, filtered through a weighed filter, and the precipitate of potassium silicofluoride (K_2SiF_6), washed with a mixture of equal volumes of alcohol and water, and dried at 100°. The sulphuric acid in the filtrate is estimated in the usual way after evaporation of the alcohol.

Titanic acid from silicic acid (*v. Silicic acid from titanic acid*).

Boric acid. The borates of the alkali and alkaline earth metals, when heated with pure methyl alcohol (free from acetone) and acetic acid, evolve all the boron present in the form of methyl borate (b.p. 65°). This liquid, when added to moist lime, is completely hydrolysed and the boric acid set free combines with the calcium oxide forming calcium borate. The decomposition is effected in a small retort fitted with a tap funnel for introducing further quantities of methyl alcohol. The retort is connected with a water condenser and a conical flask containing a weighed amount of quicklime. This lime is carefully slaked before the distillation, and the methyl borate dropping into the conical flask is decomposed and the boric acid taken up by the lime. The contents of the receiver are rinsed into a platinum dish, and the methyl alcohol evaporated at as low a temperature as possible. The residue is cautiously ignited to destroy calcium acetate, and the increase in weight of the lime represents the amount of boric anhydride B_2O_3 obtained from the borate. Instead of lime, aqueous ammonium carbonate may be used in the receiver, and the liquid poured on to slaked lime (from a known weight of quicklime) contained in a platinum dish (Zeitsch. anal. Chem. 1887, 26, 18, 364).

VOLUMETRIC METHODS.

In volumetric analysis the proportion of a substance is ascertained, not by separation and weighing, but by determining the exact volume of a reagent solution of known concentration required to produce some particular reaction, such as neutralisation, oxidation, or precipitation. The termination of the reaction is indicated by some end-reaction, which is usually a production, destruction, or change of colour, the formation of a permanent precipitate or the cessation of the formation of a precipitate. In determining the strength of caustic soda, for example, it is coloured yellow with methyl orange, and a dilute solution of sulphuric acid of known strength is added gradually until the yellow colour of the methyl orange just changes to red, thus indicating the point of neutralisation. The volume of acid required is noted; the weight of sulphuric acid which it contains, and hence the weight of soda which it will neutralise, is known, and thus the proportion of soda in the substance is determined.

In order that a reaction may serve as the basis of a volumetric process, it must be rapid, simple, and definite, and not complicated by secondary reactions. It should remain constant through considerable variations in conditions, and should not, for example, be materially affected by the degree of concentration of the solution. A final reaction should be rapid, perfectly decisive, and should only require a slight excess of the reagent for its production. In many cases a third substance is employed to indicate the completion of the reaction, and is termed an *indicator*. It is an *internal indicator* if it is added to the bulk of the liquid, an *external indicator* if drops of the liquid are removed and brought in contact with it.

The execution of volumetric processes involves the possession of accurately graduated instruments of three kinds, viz. flasks, pipettes, and burettes. The flasks should be fitted with well-ground stoppers, and should have somewhat long necks, the graduation being not higher than the middle of the neck, in order that there may be sufficient empty space for efficient agitation. Flasks holding respectively 1000 c.c., 500 c.c., 250 c.c., and 100 c.c., are used. Each flask should have two graduation marks, viz. the *containing mark*, indicating the point to which the flask must be filled in order that it may then contain the particular volume of liquid, and the *delivery mark* or point to which the flask must be filled in order that it may deliver the given volume of liquid when emptied by draining. A pipette is usually a cylindrical bulb terminating at each end in a tube, the lower of which is drawn out to a jet, whilst the end of the upper tube is slightly contracted so that it may be readily closed by the forefinger and the flow of liquid regulated or stopped altogether. Usually a pipette has only a *delivery* mark, but occasionally they are graduated throughout their whole length, and then take the form of a somewhat wide tube contracted to a jet at the bottom and terminating in a narrower tube at the top. Pipettes of 100 c.c., 50 c.c., 25 c.c., 10 c.c., and 5 c.c. capacity are most generally useful. A burette is a long tube of uniform bore, 12 to 15 mm. in diameter, graduated in cubic centimetres and tenths or fifths. A convenient capacity is 50 c.c. It is open at the top and contracted at the lower end, to which a glass jet is attached by means of a piece of narrow indiarubber tubing. This tubing is nipped by a spring pinchcock, which is opened by the pressure of the fingers, the flow of liquid being thus regulated. A better plan is to insert in the indiarubber tubing a short piece of glass rod the diameter of which is just sufficient to prevent the flow of liquid when the tubing remains circular. If, however, the tubing is squeezed out laterally by the pressure of the thumb and fore-finger (Fig. 9), a channel is made through which the liquid can pass, and by increasing or reducing the pressure, the flow of liquid can be regulated to a nicety. Certain reagents act upon indiarubber, and for these a burette with a glass stopcock should be used. This form is, in fact, the most convenient for all purposes. The stopcock may be prevented from sticking by a little vaseline or paraffin, and from slipping out by a small indiarubber ring passed over the tap and round the burette tube. Sometimes the tube carrying the stopcock is not in the same line with the burette, but is bent twice at right angles, so that the burette jet, although still vertical, is one or two inches in advance of the burette itself. This form is useful when titrating hot liquids, since the risk of heating the burette and its contents is reduced. An alternative method is to have the top of an ordinary burette funnel-shaped, which admits of the burette being slung in a stand by the funnel without other support, so that it can be tilted from the vertical when titrating hot solutions.

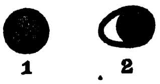


FIG. 9.

When a burette is in use, it is important that it should be supported in a vertical position. This can be done by means of a clamp attached to a stand similar to a retort stand. A useful and easily constructed burette stand is described in J. Amer. Chem. Soc. 1905, 27, 1442.

When several different solutions are being used continually, it is convenient to have the series of burettes attached to a revolving stand, so that each may be brought round to the front when required. Short test-tubes inverted over the tops of burettes serve to keep out dust.

Standard solutions should be kept in well-stoppered bottles in a cool place protected from bright light. When many determinations of the same kind have to be made, it is convenient to keep the reservoir of standard solution attached to the burette to facilitate the filling of the latter. A glass T-piece is introduced between the graduated part of the burette and the stopcock or pinchcock, and is attached by means of an indiarubber tube to a tubulus at the bottom of the bottle which contains the standard solution and stands on a shelf above the burette. If this bottle has no tubulus, a glass tube bent twice at right angles, with one limb reaching to the bottom of the bottle and the other connected with the burette, is fitted into the neck of the bottle by means of a cork, and is kept always full, so that it acts as a siphon. There must, of course, be an entrance for air as the liquid flows from the bottle. The flow of liquid into the burette is regulated by a pinchcock on the indiarubber tube. If the standard solution acts upon indiarubber, all these connections must be constructed of glass tubing. Burettes may now be obtained fitted with Greiner and Friedrich's three-way taps (compare Fig. 12); these are readily connected to reservoirs and filled from the bottom. Filling the burette from the bottom avoids the formation of air-bubbles, but it can also be filled from the top if the tube from the stock bottle is bent slightly so that the liquid flows down the side of the burette. A convenient form of apparatus for this method, which is the only one available with an ordinary tap burette without a side-tube attachment, is described in Chem. News, 1906, 93, 71. When the standard solution alters if exposed to air, the surface of the liquid may be covered with a layer of rectified paraffin of moderately high boiling-point, or the neck of the bottle may be provided with a cork carrying a tube containing caustic potash, or alkaline pyrogallate, through which all air entering the bottle has to pass. A still better plan is to fill the upper part of the stock bottle with carbon dioxide, or, if the nature of the solution permits, with coal gas, and connect it by means of a cork and tube with a self-acting carbon dioxide apparatus or the ordinary gas supply. When solution is withdrawn, carbon dioxide or coal gas enters. The burette should be kept permanently attached to the reservoir as just described, and the top end of the burette also put into communication with the inert gas supply.

Graduation of the instruments.—Accurate calibration of the measuring vessels is of course necessary if correct results are to be obtained, and it is never advisable to trust the makers' graduations. All the instruments should be checked before being taken into use. Although it is sufficient for most purposes if the relative volumes of the vessels are correct, they should nevertheless be graduated in true cubic centimetres. With gas-volumetric apparatus this procedure is essential. If the calibration is performed at a temperature of 18°–20°, variations from the true volume resulting from the expansion of the glass are so small for the intervals of temperature through which the laboratory is likely to vary, that they may be neglected.

The vessels are checked by ascertaining the weight of distilled water at a known temperature which they will contain or deliver as the case may be. A large beaker of distilled water is placed in the balance room, and left for some hours till its temperature has become constant. The vessels to be calibrated are thoroughly cleansed by successive treatments with concentrated caustic potash, distilled water, and a warm solution of chromic acid in concentrated sulphuric acid, and then rinsed well with distilled water. The flasks are then dried. A narrow strip of paper is attached vertically to the neck of the litre flask near the mark, the flask placed on one pan of a large balance capable of responding to 0·05 gram, and counterpoised. Weights corresponding with the weight of water which at the temperature of the supply in use will occupy 1000 c.c., are then placed in the pan; the flask is filled nearly to the mark with water, and water is gradually added until flask and weights are in equilibrium. Any water adhering to the inside of the neck of the flask above the mark must be removed by means of filter paper. If the mark on the neck of the flask is thus found to be in error, a pencil mark is made on the strip of paper at the point corresponding with the lower edge of the meniscus, the glass above and below is evenly coated with a thin film of wax, and a horizontal ring is scratched through by means of a needle precisely on a level with the pencil mark. The ring is covered with a small piece of filter paper, which is moistened with hydrofluoric acid, care being taken to remove air-bubbles. After a few minutes the acid is washed off and the wax removed, when a new mark will be found etched into the glass.

In calibrating volumes by determining weights of water, it is necessary to reduce the weight to vacuum standard, and then divide the result by the density of the water in order to obtain accurately the volume in true cubic centimetres. This calculation can be avoided by making use of the following table:—

t°	0°	1°	2°	3°	4°	5°	
x	1·19	1·13	1·09	1·07	1·06	1·07	
t°	6°	7°	8°	9°	10°	11°	
x	1·09	1·13	1·18	1·25	1·33	1·43	
t°	12°	13°	14°	15°	16°	17°	
x	1·53	1·65	1·78	1·93	2·09	2·25	
t°	18°	19°	20°	21°	22°	23°	
x	2·43	2·62	2·82	3·03	3·26	3·49	
t°	24°	25°	26°	27°	28°	29°	30°
x	3·73	3·98	4·24	4·52	4·80	5·08	5·38

x is the quantity to be subtracted from 1000 to obtain the apparent weight (in air, when brass weights are employed) of 1000 c.c. of water at the temperature t. For example, at 18° the apparent weight of 1000 c.c. is $1000 - 2{\cdot}43 = 997{\cdot}57$ grams.

The litre flask having been graduated to contain, it should now be graduated to deliver. The full flask is carefully emptied and allowed to drain for a definite time—say thirty seconds—again counterpoised with the water adhering to the inside, and again filled with a further 1000 c.c. of water in the manner previously described. The other flasks are graduated in the same way, subtracting only $\frac{1}{2}x$ from 500 grams in the case of the 500 c.c. flask, $\frac{1}{4}x$ from 250 grams for the 250 c.c. flask and so on.

The quantity of liquid which a pipette will deliver depends to some extent on the manner in which it is emptied. A small quantity of liquid always remains in the jet, and this should not be blown out. The best plan is to allow the pipette to empty itself whilst held vertically, and then to let it drain for twenty seconds with the point of the pipette just touching the side of the receiving vessel; but the method of emptying employed in the calibration must be adhered to in its subsequent use.

To test the accuracy with which a pipette has been graduated, it is filled to the mark with distilled water at an observed temperature, the contents delivered into a light, tared, stoppered flask, and accurately weighed. The operation is repeated several times, and from the mean result the true volume is calculated by using the table previously given; for it is clear that $1 - \frac{x}{1000}$ denotes the apparent weight of 1 c.c. of water at $t°$, or $1 + \frac{x}{1000}$ equals the volume at $t°$ occupied by 1 gram of water weighed in air with brass weights. If the error in graduation is greater than can be allowed, another mark must be made; its position may be found by repeated trials, a strip of paper being pasted along the stem, and the volumes corresponding to various pencil marks being found as above. The new mark is then etched in with hydrofluoric acid.

A convenient method for directly calibrating pipettes is described by Thorpe (Quantitative Analysis). The pipette is suspended from one arm of a balance by means of a clip, so as to hang perpendicularly and pass through a hole in the bottom of the balance case or of a specially constructed table. A suitable clip (Fig. 10) consists of a stout brass wire frame carrying two clips of sheet brass closed by sliding collars. The upper end of the pipette is passed through the lower clip and connected by caoutchouc tubing with a glass stopcock fixed in the upper clip. The other end of the stopcock is provided with a piece of caoutchouc tubing, to which a piece of thermometer tube or a piece of wider glass tube can be attached. The wider glass tube, which serves as a mouthpiece, is first attached to the stopcock, and the pipette is filled with water to a short distance above the mark, and then emptied by the method to be adopted in its subsequent use. It is then counterpoised on the balance with the adhering water inside, the wide tube being replaced by the thermometer tube, and the requisite weights placed on the other pan. The pipette is again filled to a short distance above the mark; the thermometer tube, which is drawn out at one end, is attached again, and the stopcock is opened. Water drops very slowly from the end of the pipette, and it can be arrested the moment the balance is in equilibrium. The level of the water is marked on a piece of paper gummed to the pipette, and a new ring etched with hydrofluoric acid.

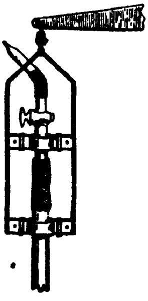


FIG. 10.

The burette is most simply calibrated by the method due to Ostwald with the help of a small pipette of about 2 c.c. capacity, attached to the burette as indicated in Fig. 11. The burette and pipette are filled with water to the zero mark and the mark a respectively, taking care to leave no air bubbles in the tubes. The clip I (or the tap of the burette) is opened and water allowed to run from the burette into the pipette till the level b is reached. The burette reading is then noted, and the pipette emptied to mark a. These operations of filling the pipette, taking a burette reading, and then emptying the pipette, are repeated to the full extent of the burette readings. Suppose, for example, that after twenty-four fillings the burette reading is 49·49 c.c. The burette is now refilled, and exactly this amount of distilled water is run out into a tared flask and weighed, using all the precautions that would be observed in an actual titration. From the table already given the true volume of this water is calculated. Suppose this to be 49·44 c.c. Then the volume of the calibrating pipette must be $\frac{49{\cdot}44}{24} = 2{\cdot}060$ c.c. The differences between the successive burette readings and the successive numbers 2·06, 4·12, 6·18 . . . give at once the burette errors at these intervals, due regard being paid to the sign of the difference. In the example quoted, the correction to be applied for 50 c.c. is obviously $-0{\cdot}05$ c.c. (*see* J. Amer. Chem. Soc. 1900, 22, 149; and for a modification of above, J. Amer. Chem. Soc. 1901, 23, 484).

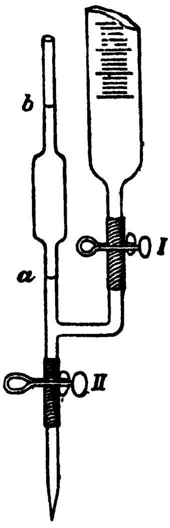


FIG. 11.

A better design for a calibrating pipette is shown in Fig. 12, which also illustrates the Greiner and Friedrich three-way tap (Morse and Blalock, Amer. Chem. J. 1894, 16, 479).

The gas burettes described under *Gas analysis* may be calibrated in much the same way as an ordinary burette, by filling with water or mercury, drawing off aliquot portions and weighing them, the temperature of the liquid being noted and the appropriate correction made for expansion. Any error thus detected must be used as a correction in subsequent readings.

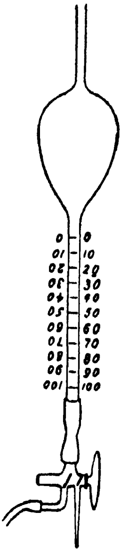


FIG. 12.

Standard solutions. — These form the basis of all volumetric work, and great care should be exercised in their preparation. When a solution is used only for the estimation of one substance, it may be convenient to adjust its strength so that each c.c. is equivalent to some simple and definite quantity of the substance, say 0·01 gram; but for general purposes the so-called *normal solutions* should be employed. A *normal solution* contains in 1000 c.c. the equivalent in grams of the active substance. A solution of one-tenth this strength is termed a *decinormal* solution, and one of a hundredth a *centinormal* solution. Thus a normal solution of sulphuric acid contains 49·04 grams of real acid per litre, a decinormal solution of iodine contains 12·69 grams of iodine per litre, and each litre of a decinormal solution of potassium permanganate contains 0·8 grams of active oxygen.

Standard solutions are usually made up approximately normal or decinormal as the case may be, and afterwards accurately standardised by titration against a weighed amount of some pure compound. If the solution has been purposely made rather too concentrated, it may then be suitably diluted until exactly normal or decinormal. Since accurate adjustment by dilution is difficult to effect, and in a certain cases inadvisable, it is usually better to avoid the process and determine *a factor* by which readings must be multiplied in order to convert them into equivalent readings of a normal or decinormal solution. For example, if 1 c.c. of potassium permanganate solution is found to be capable of oxidising 0·005630 grams of iron, then since the corresponding figure for a decinormal solution is 0·005585, the permanganate is $\frac{5630}{5585}$, or 1·008 times decinormal, and when using it to estimate a substance of equivalent x, each c.s. of permanganate will oxidise $\frac{x}{10000} \times 1{\cdot}008$ grams of substance. When only one or two litres of a standard solution are required, and the pure reagent is at hand, the exact quantity may be weighed out and diluted to the appropriate volume; *e.g.* solutions of silver nitrate and potassium dichromate may be thus prepared.

Measurements.—In measuring out solutions, &c., the vessels must be perfectly dry, which is inconvenient, or must be well drained and then rinsed out with a small quantity of the solution to be measured, which is allowed to run away.

To read correctly the level of the liquid in a burette or pipette requires certain precautions. In the first place, the instrument must be held in a vertical position. Ordinary liquids form a concave surface, or meniscus, and the reading should always be taken from the lowest point of this curve, except in the case of very dark-coloured solutions, when the upper line of the surface must be taken. The meniscus must be properly illuminated, and on a level with the eye, in order to avoid parallax. The best method of avoiding this error is by the use of a burette having the graduation marks carried half-way round the tube. In default of such a burette, use may be made according to Mohr of a piece of card one-half of which is black and the other half white. This is attached to the burette by an indiarubber ring, and is adjusted so that the horizontal edge of the black half, which is lowest, is 2 to 3 mm., *but not more,* below the meniscus. The lower edge of the curve then appears black against the white background. If the card is too low, the reading will be slightly too high. The little clamp and screen designed by Göckel are based on the same principle. Some burettes are provided at the back with a dark vertical line on a milk glass background. When the eye is on a level with the bottom of the meniscus, the dark line appears to be drawn out to two fine points which just touch one another. By means of these devices accurate readings can easily be taken even without using a burette float.

In addition to the errors incident to all analytical processes, another error arises in volumetric analysis, owing to variations in the concentrations of the solutions due to changes of temperature. In the case of $N/10$-solutions this affects the results to the extent of 0·1 p.c. for each 5° variation in temperature. With concentrated solutions, especially those of the acids and alkalis, the error is greater. The coefficients of expansion of certain standard solutions have been determined by A. Schulze (Zeitsch. anal. Chem. 21, 167).

Errors due to changes of temperature may be eliminated by weighing the solutions instead of measuring them. The liquid is contained in a light glass bottle, with a long jet-like neck, and a tubulus at the shoulder which can be closed by the finger, and the flow of liquid thus regulated. The bottle is weighed, the solution poured gradually from it until the reaction is complete, and the bottle again weighed. The difference between the two weighings gives the quantity of solution used. Convenient weight burettes are described in Chem. News, 1877, 35, 98; J. Amer. Chem. Soc. 1908, 30, 31.

Volumetric methods may be broadly classified as I. Methods of Saturation; II. Methods of Oxidation and Reduction; III. Methods of Precipitation; and examples of the two latter types of processes are indicated below. (For methods of saturation, *v.* ACIDIMETRY AND ALKALIMETRY.)

In the following section the methods for preparing and standardising the more commonly employed solutions are first described, followed by details of the various volumetric estimations for which these solutions may be conveniently employed, alphabetically arranged under the names of the elements that are determined.

PREPARATION OF STANDARD SOLUTIONS.

Potassium permanganate.

Employed as an oxidising agent, usually in dilute sulphuric acid solution, when the permanganate decomposes according to the equation:

$$2KMnO_4+3H_2SO_4 \\ =K_2SO_4+2MnSO_4+3H_2O+5O.$$

The oxidation of ferrous sulphate, for example, is represented in the following manner:—

$$2KMnO_4+10FeSO_4+8H_2SO_4 \\ = K_2SO_4+2MnSO_4+5Fe_2(SO_4)_3+8H_2O$$

and of oxalic acid thus:

$$2KMnO_4+5H_2C_2O_4+3H_2SO_4 \\ = K_2SO_4+2MnSO_4+8H_2O+10CO_2.$$

In order to facilitate calculation, these oxidations are conveniently expressed as a transference of oxygen from one oxide to another, *e.g.*:

$$10FeO+Mn_2O_7 = 5Fe_2O_3+2MnO.$$

The utility of permanganate solution depends upon the facts that such oxidation processes are usually quite easy to effect, the end-point being readily indicated by the solution acquiring a faint permanent pink tinge, due to the presence of a slight excess of permanganate, which thus acts as its own indicator. Oxidation usually proceeds rapidly at the ordinary temperature, but solutions of oxalic acid must be heated to 60°–80°. It is most essential that a considerable excess of sulphuric acid should be present (about 5 c.c. of concentrated acid per 100 c.c. of solution), since otherwise the solution becomes turbid owing to the separation of manganese dioxide, and the determination is spoilt. The presence of hydrochloric acid in the solution should be avoided, if possible, since it reacts with the permanganate under certain circumstances, particularly in the presence of iron salts. The error that thus arises can be reduced to a negligible amount by adding manganese sulphate to the solution, and titrating very slowly. The addition of colloidal silicic acid, added in the form of a solution of sodium silicate, containing about 0·1 gram SiO_2 per 1 c.c., entirely prevents the oxidation of the hydrochloric acid in presence of manganous sulphate.

Preparation and titration of the solution.—A decinormal solution containing 3·16 grams of the salt per litre of solution is most convenient for general use; it is most readily prepared by grinding the solid repeatedly with small amounts of distilled water in a mortar and decanting the solution into the stock bottle. After a day or two, the solution is filtered through asbestos, and standardised. If kept away from direct sunlight, reducing gases and dust, it retains its titre for a long time; its spontaneous decomposition is largely augmented by the presence of solid dioxide, which explains the necessity for the filtration through asbestos (Amer. Chem. J. 1896, 18, 401).

The solution is best standardised against electrolytic iron, anhydrous sodium oxalate, or by the iodimetric method of Volhard, using a thiosulphate solution which has been recently titrated against pure iodine. (For the latter method, *see Thiosulphate solution*, and for the first, which requires a somewhat complicated apparatus, consult Treadwell-Hall, vol. 2, 81.)

Titration by sodium oxalate.—This method was proposed by Sörensen, and its accuracy has been fully established by various other chemists (Zeitsch. angew. Chem. 1902, 15, 1244; 1904, 17, 230 and 269; 1905, 18, 1520). The pure oxalate, prepared by Kahlbaum according to Sörensen's directions, should be dried at 100° for a few hours before use.

Three or four portions of the oxalate, each weighing about 0·25–0·30 grams, are dissolved in an excess of dilute sulphuric acid; the solutions are warmed to 60°–80°, and titrated with the permanganate solution until a faint, permanent pink colouration is obtained. From the relation $2Na_2C_2O_4 = O_2$, the value of the permanganate solution is calculated for each titration, and the mean of the concordant results adopted as the true value (*cf* McBride, J. Amer. Chem. Soc. 1912, 34, 393).

Many other methods for standardising permanganate have been proposed, *e.g.* titration against crystalline oxalic acid $H_2C_2O_4,2H_2O$, ammonium oxalate $(NH_4)_2C_2O_4,H_2O$, ferrous sulphate $FeSO_4,7H_2O$, Mohr's salt $FeSO_4.(NH_4)_2SO_4,6H_2O$, &c., which although at times convenient, are less accurate than the methods given. Standardisation against iron wire is not to be recommended, since the small quantities of oxidisable impurities present consume more permanganate than would be required by their own weight of iron, and the error is augmented by making allowance for the actual iron content of the wire (Zeitsch. anal. Chem. 1903, 42, 359; Zeitsch. angew. Chem. 1901, 14, 1233; also Treadwell-Hall, *l.c.*).

It is usual to express the concentration of a permanganate solution in terms of the amount of iron it can oxidise; thus 1 c.c. of *N*/10-$KMnO_4$ = 0·005585 gram Fe.

Potassium dichromate.

A solution of this reagent may replace permanganate in the titration of ferrous salts, with the advantage that it can be used in the presence of either hydrochloric or sulphuric acid. An excess of free acid is essential, the oxidation of ferrous chloride, for example, proceeding according to the equation:

$$K_2Cr_2O_7+6FeCl_2+14HCl \\ = 2KCl+2CrCl_3+6FeCl_3+7H_2O$$

which is essentially:

$$2CrO_3+6FeO = Cr_2O_3+3Fe_2O_3.$$

A decinormal solution obtained by dissolving $\frac{K_2Cr_2O_7}{60} = 4·903$ grams of the pure dry recrystallised salt in distilled water and diluting the solution to 1 litre, requires no further standardisation. A stock solution of approximate strength may be standardised against several weighed amounts (1·0–1·4 grams) of pure ferrous ammonium sulphate by a similar procedure to that described under the standardisation of permanganate by sodium oxalate. The titrations, however, are made in cold solution, and the dilute sulphuric acid used should be gently boiled for half an hour to expel dissolved air, and cooled rapidly just before use. Since the green colour of the chromic salt prevents the excess of dichromate from being seen, an external indicator is necessary. Drops of a *dilute* solution of potassium ferricyanide, free from ferrocyanide, are placed on a white plate, and from time to time the end of a glass rod, previously dipped in the titrating flask, is brought into contact with a drop of the ferricyanide. As long as any ferrous salt remains a blue precipitate is produced; the approach of the end is indicated by the decrease in intensity of the blue colouration, and when very near the end about thirty seconds should be allowed for the colour to develop. The end-point is reached when the blue colour ceases to appear. The ferricyanide solution should be prepared only when required by dissolving in water a crystal of the salt which has been rinsed to remove superficial ferrocyanide: the yellow colour of the drops on the white plate should be barely visible; if the ferricyanide is too concentrated, the blue colouration changes through various shades of green into a brown tint.

Iodine, Sodium thiosulphate, and Sodium arsenite.

Decinormal solutions of these reagents are frequently used in conjunction with one another. The reaction between iodine and sodium thiosulphate is essentially:

$$2Na_2S_2O_3+I_2 = Na_2S_4O_6+2NaI$$

although under certain circumstances oxidation to sulphate proceeds to a small extent, even at the ordinary temperature (Pickering). When using decinormal solutions the end-point is readily indicated by the appearance or disappearance of the yellow colour of the iodine, provided the solution undergoing titration is not unduly diluted and is otherwise colourless. The production of a blue colour when free iodine and starch solution are brought together is, however, much more sensitive, and is the method usually employed in ascertaining the end-point.

Preparation of starch solution.—About 1 gram of powdered starch is rubbed into a paste with a little cold water, and slowly added to 200 c.c. of boiling water, the boiling is continued for two or three minutes, the solution cooled, and after some hours the clear liquid is decanted. The solution will only keep for one or two days, unless sterilised, when it is conveniently preserved in small bottles, completely filled and closed by soft rubber stoppers; it will then keep indefinitely. Starch paste prepared from Gastine's formula (5 grams starch, 0·01 gram mercuric iodide, and 1 litre water) retains its sensitiveness for a long time. Addition of 1 c.c. of oil of cassia to a litre of starch liquor is also recommended as a preservative.

Sensitiveness of the iodine-starch reaction.—This depends upon several circumstances. It is necessary to work with cold solutions, preferably neutral or slightly acid; the presence of mineral acid in high concentration greatly impairs the sensitiveness of the reaction, since it hydrolyses the starch. It is essential that a soluble iodide should be present (usually this is potassium iodide) in moderate amount; the best concentration of potassium iodide to employ is about *N*/150, since the sensitiveness of the reaction then reaches a maximum (*see* Zeitsch. anal. Chem. 1902, 41, 485; Amer. J. Sci. 1900, [iv.] 10, 151; J. Amer. Chem. Soc. 1909, 31, 1038).

Good starch solution first yields a pink colouration with iodine, which more iodine develops into the blue colour; starch which produces green tints should be rejected (J. Amer. Chem. Soc. 1908, 30, 31). It frequently happens in titrating arsenious and antimonious oxides with iodine that various tints of red make their appearance instead of the usual blue colouration. This is due to impurity in the starch: in such a case one or two grams of potassium iodide are added, the end-point being ascertained from the development of the yellow colour of the iodine, and then confirmed by the starch (Amer. J. Sci. 1902, [4] 13, 379).

Sinnatt (Analyst, 1910, 35, 309) has shown that 1 c.c. of a dilute aqueous solution of methylene blue (0·05 gram per litre) may be used in place of starch as an indicator in iodimetric titrations (*see* also Analyst, 1912, 37, 252).

For the *iodine solution* 25 grams of potassium iodide are dissolved in a little water, 12·7 grams of commercial iodine added, and the mixture shaken till the iodine has dissolved; the solution is then filtered through asbestos and diluted to 1 litre. It should be kept in the dark, and protected from dust. For the *thiosulphate solution* the crystalline salt $Na_2S_2O_3,5H_2O$ is dissolved in distilled water, using 25 grams per litre, and the solution kept away from direct sunlight for two weeks before it is standardised. It then retains its titre for months. For the *sodium arsenite*, 4·948 grams of resublimed arsenious oxide are dissolved in a little warm sodium hydroxide free from iron, the solution rinsed into a litre flask, and made just acid to phenolphthaleïn with dilute sulphuric acid. A filtered solution of 20 grams of sodium bicarbonate in 500 c.c. of water is added, and if the mixture reacts alkaline to the phenolphthaleïn, sulphuric acid added till the pink colour disappears. This solution, when diluted to 1 litre and thoroughly mixed, is strictly decinormal, and keeps indefinitely. A measured quantity of the *N*/10-arsenite solution is delivered into an Erlenmeyer flask, and the iodine solution run in from the burette until present in slight excess, starch paste being added nearly at the finish of the titration (*see* remarks on starch above). The reaction

$$As_2O_3+2I_2+2H_2O \rightleftharpoons As_2O_5+4HI$$

proceeds to completion in the sense of the upper arrow in neutral solution, a condition secured by the presence of the bicarbonate, which neutralises the hydriodic acid produced. Since the solution should be saturated with carbon dioxide, it is advisable to stopper the flask except when actually introducing the iodine (J. Amer. Chem. Soc. 1908, 30, 31).

The iodine being standardised, the thiosulphate can be directly titrated against it, preferably by running the iodine into a measured volume of thiosulphate.

Many alternative methods have been proposed for standardising iodine and thiosulphate solutions. The latter may be titrated against pure iodine: 0·5 gram of pure iodine and 0·1 gram of potassium iodide are powdered and mixed together in a porcelain dish, and heated on a sand-bath till vapour is copiously evolved; the dish is then covered with a dry watch-glass, and the greater part of the iodine sublimed on to it. The watch-glass is covered with a second accurately fitting glass and the whole weighed, the weight of the glasses having been previously found. The whole is gently placed in a solution of 1 gram of potassium iodide in 10 c.c. of water, and after a few seconds the solution is diluted to 100 c.c. and titrated with the thiosulphate.

The thiosulphate may also be standardised against permanganate, itself verified by reference to sodium oxalate. One or two grams of potassium iodide are dissolved in water, acidified with 5 c.c. of hydrochloric acid (1 : 5) and 25 c.c. of standard permanganate added. The iodine, which is quantitatively liberated:

$$Mn_2O_7 + 10HI = 2MnO + 5H_2O + 5I_2$$

is then titrated with the thiosulphate, after diluting the solution to 100 c.c. By the reverse process of calculation, a permanganate solution may be standardised against a thiosulphate solution that has been verified by either of the preceding methods (*see Standardisation of permanganate; cf.* Annalen, 1897, 198, 333; Zeitsch. angew. Chem. 1904, 17, 815; Ann. Chim. Anal. 1904, 9, 365; Zeitsch. anorg. Chem. 1906, 49, 277).

(For the use of potassium dichromate in this connection, *see Volumetric estimation of chromium*: Zeitsch. anorg. Chem. 1899, 19, 427; 1906, 49, 277. *See* also *Copper* under *Volumetric estimations*. For a gravimetric method for standardising iodine solution, consult Amer. J. Sci. 1909, (iv.) 28, 33.)

Titanous chloride.

This reagent, introduced into volumetric analysis by Knecht (J. Soc. Dyers and Colourists, 19, No. 6; Ber. 1907, 40, 3819), is a powerful reducing agent. For example, a hydrochloric acid solution of ferric chloride is quickly and quantitatively reduced in the cold, according to the equation:

$$FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4$$

and the end-point is reached when a drop of the liquid ceases to produce a red colouration with potassium thiocyanate. Chromic acid and cupric salts may be similarly estimated, and also a large number of organic dyes.

Fifty c.c. of the commercial 20 p.c. solution of titanous chloride, which usually contains a little iron, are mixed with an equal volume of concentrated hydrochloric acid, boiled for several minutes, and diluted to 1 litre with air-free water. The solution must be kept protected from the air; a convenient method is figured in Sutton's Volumetric Analysis (9th ed.), p. 224.

The concentration of the solution is fixed by titrating against a known quantity of either ferric salt or potassium dichromate. In the former case 35 grams of pure ferrous ammonium sulphate are dissolved in dilute sulphuric acid and the solution diluted to 1 litre; 25 c.c. are then exactly oxidised with dilute permanganate, and the resulting ferric sulphate titrated with the titanous chloride until a drop of the solution no longer gives a red colour with potassium thiocyanate. Instead of using this 'spot-out' method, 10–20 c.c. of 10 p.c. potassium thiocyanate may be added to the ferric solution. If the standardisation be effected with potassium dichromate, addition of the indicator to the solution itself is inadmissible. Nearly all the titanous chloride necessary, may, however, be added at once, since the colour changes, through orange to green and then violet, afford an indication of the end-point. Drops of solution are removed for testing when the green colour has just disappeared (J. Soc. Chem. Ind. 1908, 27, 673).

Pure ferric alum, the preparation of which is described by De Koninck (Bull. Soc. chim. Belg. 1909, 23, 222), might also be employed for this standardisation.

For a number of estimations it is necessary to employ titanous sulphate instead of the chloride.

Stannous chloride.

This reagent has long been employed as a reducing agent, but the closely allied and more powerfully reducing titanous salts appear to be displacing it. Ferric salts are easily reduced in hot acid solution:

$$2FeCl_3 + SnCl_2 = SnCl_4 + 2FeCl_2.$$

Iodine in cold acid solution oxidises it quantitatively:

$$2SnCl_2 + 2I_2 = SnI_4 + SnCl_4.$$

Ten grams of pure tin in thin pieces are heated with 200 c.c. of concentrated hydrochloric acid in a platinum dish until dissolved: or a glass flask may be used with a piece of platinum foil touching the tin to promote its speedy solution. The solution is diluted to 1 litre, and preserved out of contact with the air.

The solution is best standardised by that process for which it is afterwards to be employed, *e.g.* if required for iron estimations, by titration against a known amount of ferric chloride. The latter may be obtained by dissolving 10·03 grams of bright iron wire (99·7 p.c. iron) in hydrochloric acid, oxidising with potassium chlorate, expelling the excess of chlorine by boiling, and diluting the solution to 1 litre; 25 c.c. are conveniently used for titrating the above solution.

Several methods have been proposed for determining the end-point. The iron solution containing 20–40 c.c. of concentrated hydrochloric acid in a volume of 125 c.c. may be titrated nearly at the boiling-point, 15 c.c. of indicator solution (34 grams $HgCl_2$+0·05 gram Pt as chloride per litre) being added. The end-point is reached when a dark-cloud of finely divided mercury and platinum is produced (Amer. Chem. J. 1893, 15, 360). Or a drop of the solution may be mixed with ammonium molybdate on a white plate; the slightest trace of stannous salt causes a blue colouration. An alternative is to add a slight excess of stannous chloride, and titrate back the cold solution with iodine.

(For the standardisation by means of iodine, *see Volumetric estimation of tin.*)

Silver nitrate, Sodium chloride, and Ammonium thiocyanate.

These precipitation reagents, which are conveniently made of decinormal strength, are of great service for the volumetric estimation of silver, copper, mercury, the halogen acids, cyanides, and thiocyanates.

Silver nitrate is used either in neutral or in nitric acid solution. In the first case potassium chromate is employed as indicator when halogens are being estimated (Mohr's method). Silver chromate is decomposed by solutions of halogen salts forming silver halide and metallic chromate; consequently, silver chromate cannot permanently exist in the solution until all the halogen has been precipitated. The first drop of silver nitrate in excess then produces a permanent precipitate of silver chromate, which gives a faint red tint to the previously pale-yellow liquid. This colour change is more readily observed in monochromatic light (from a powerful sodium flame). One or two drops of a 10 p.c. solution of potassium chromate are added to the solution, which should not be unduly diluted. Silver chromate is soluble in mineral acids or ammonia; hence the necessity for working in neutral solution. An alkaline solution may be acidified with dilute nitric acid, and then neutralised with powdered calcium carbonate. Barium must be absent from the solution, since it precipitates the indicator; it may be removed with sodium sulphate.

In the presence of nitric acid, silver nitrate and ammonium thiocyanate solutions are used in conjunction (Volhard's method, Annalen, 1878, 190, 47). The addition of thiocyanate to a nitric acid solution containing silver causes the precipitation of white silver thiocyanate, and the end-point is indicated by the red colouration produced by the interaction of the first drop of thiocyanate in excess with a ferric salt previously introduced into the solution. The thiocyanate should always be added to the silver solution. The ferric indicator is prepared by adding nitric acid (4 : 1 boiled to expel nitrous acid) to a saturated solution of iron alum until colourless; 5–10 c.c. are used in the titration.

Standard sodium chloride solution is used for the estimation of silver by the very exact method originally due to Gay-Lussac. (For a description of the method, *v.* ASSAYING.)

Decinormal silver nitrate is obtained by dissolving 16·99 grams of the pure dry recrystallised silver nitrate in water and diluting the solution to 1 litre. If it is to be used in conjunction with the thiocyanate, this solution may also be prepared by dissolving 10·788 grams of pure silver in a slight excess of nitric acid, boiling till nitrous acid is expelled, and diluting to 1 litre.

The thiocyanate is prepared approximately decinormal by dissolving the salt in distilled water (8 grams per litre), and is standardised against the silver nitrate solution, 25 c.c. of which are diluted to 100 c.c. and titrated as described above.

VOLUMETRIC ESTIMATIONS.

Aluminium. *Iodimetrically.* The neutral solution is boiled with excess of potassium iodide and potassium iodate for twenty minutes in a stream of hydrogen; the iodine evolved, and collected in potassium iodide, together with that which remains in the distilling flask, is titrated with *N*/10-thiosulphate (Amer. J. Sci. 1905, 20, 181; Zeitsch. anorg. Chem. 1907, 52, 286):

$$Al_2(SO_4)_3+5KI+KIO_3+3H_2O$$
$$=2Al(OH)_3+3K_2SO_4+3I_2.$$

Antimony. ANTIMONIOUS SOLUTIONS. (*a*) *Iodimetrically.* One or two grams of Rochelle salt are added, the solution made alkaline with sodium bicarbonate, and titrated with *N*/10-iodine. I_2 = Sb (*v.* ARSENIC).

(*b*) *By oxidation.* The hot hydrochloric acid solution (above 60°) is titrated with *N*/10-potassium bromate, which has been standardised against a known amount of pure antimony—

$$3SbCl_3+KBrO_3+6HCl=3SbCl_5+KBr+3H_2O.$$

The end-point is indicated by the bleaching of a few drops of methyl orange added to the hot solution (Chem. Zeit. 1903, 27, 749; J. Soc. Chem. Ind. 1906, 25, 1181; Chem. News, 1907, 95, 49).

(*c*) *By oxidation.* The cold solution, freely acidified with hydrochloric acid, is titrated with *N*/10-permanganate (Zeitsch. angew. Chem. 1901, 14, 1179; J. Amer. Chem. Soc. 1907, 29, 66).

ANTIMONIC SOLUTIONS. (*a*) *By reduction* to the tervalent state, and estimation by one of the foregoing processes. Reduction may be accomplished: (i.) by boiling the hydrochloric acid solution with sodium sulphite or sulphurous acid (Zeitsch. angew. Chem. 1888, 155); according to Rohmer, the reduction is not quantitative unless a gram of potassium bromide is added (Ber. 1901, 34, 1565); (ii.) by boiling the sulphuric acid solution (100 c.c. containing 5 c.c. of concentrated acid and 4 grams of Rochelle salt) with 1·0–1·5 grams of potassium iodide till nearly all the iodine is expelled, exactly bleaching the remainder with dilute sulphurous acid, diluting, rapidly cooling, and neutralising. The solution is then titrated in bicarbonate solution with *N*/10-iodine (Amer. J. Sci. 1892, 42, 213).

(*b*) *Iodimetrically.* The cold solution containing 20–25 c.c. of hydrochloric acid in a volume of 100 c.c., is mixed with 0·5–1·0 gram of potassium iodide and the liberated iodine titrated with *N*/10-thiosulphate. I_2 = Sb (Zeitsch. anorg. Chem. 1908, 58, 202; cf. *ibid.* 1903, 37, 337).

Arsenic. ARSENIOUS SOLUTIONS. *Iodimetrically.* The solution, containing sodium bicarbonate in excess, is titrated with *N*/10-iodine as described under the standardisation of iodine solution. The bicarbonate may with advantage be replaced by disodium hydrogen phosphate (J. Amer. Chem. Soc. 1908, 30, 31).

ARSENIC SOLUTIONS. (*a*) *By reduction* with hydriodic acid as described under *Antimony*, and subsequent titration with iodine; no Rochelle salt is necessary (Amer. J. Sci. 1900, 10, 151). Reduction may also be effected by heating the sulphuric acid solution with sulphurous acid in a stoppered bottle for an hour, diluting and boiling down to half the volume to expel excess of sulphurous acid (Zeitsch. anal. Chem. 1883, 22, 378; Chem. News, 1886, 53, 221).

(*b*) *By precipitation.* The neutral or acetic acid solution is precipitated with excess of silver nitrate, and the precipitated silver arsenate collected, washed, dissolved in nitric acid, and the silver titrated with *N*/10-thiocyanate. 3Ag = As.

(*c*) *Iodimetrically* (Zeitsch. anal. Chem. 1906, 45, 596; compare Amer. J. Sci. 1900, 10, 151). (*See* also Zeitsch. anorg. Chem. 1909, 62, 123, for a method suitable for small quantities of arsenic.)

Barium. *Iodimetrically.* Excess of potassium iodate is added to the faintly ammoniacal solution, the precipitated iodate washed with ammonia and then with alcohol, dissolved in hydrochloric acid and potassium iodide, and the iodine titrated with $N/10$-thiosulphate. $6I_2=Ba$ (J. Amer. Chem. Soc. 1909, 31, 43).

Bismuth. (*a*) *Iodimetrically.* The solution, as free as possible from mineral acids, is mixed with excess of $N/2$-potassium chromate, shaken for 10 minutes, diluted to a known volume, and the chromate in an aliquot part of the filtrate from the bismuthyl chromate $Bi_2O_3 \cdot 2CrO_3$ is titrated iodimetrically (Zeitsch. anorg. Chem. 1902, 32, 362; Zeitsch. anal. Chem. 1907, 46, 223).

(*b*) As *bismuth ammonium molybdate* (J. Amer. Chem. Soc. 1903, 25, 907).

Boron. (*a*) *v.* ACIDIMETRY AND ALKALIMETRY.

(*b*) *Iodimetrically.* The reaction

$$5KI+KIO_3+6HBO_2=3I_2+3H_2O+6KBO_2$$

is quantitative in a solution saturated with mannitol (*v.* Amer. J. Sci. 1899, 8, 127).

Bromine *v. Halogens.*

Calcium. *By oxidation.* The oxalate, precipitated from a hot slightly ammoniacal solution (*see Gravimetric methods*), is washed with warm water till free from ammonium oxalate, decomposed with hot dilute sulphuric acid, and the oxalic acid titrated with $N/10$-permanganate. The precipitate may also be dissolved in dilute hydrochloric acid, 0·5 gram of manganese sulphate added, and the solution titrated with permanganate (*v.* Amer. Chem. J. 1905, 33, 500).

Carbon. CARBON DIOXIDE. *v.* ACIDIMETRY and ALKALIMETRY, and *Gas analysis.*

CYANOGEN ACIDS. CYANATES. The cold, dilute solution is exactly neutralised with $N/10$-hydrochloric acid (using methyl orange or congo red as indicator), excess of acid is added, the solution boiled for ten minutes, cooled and titrated back $N/10$-sodium hydroxide. Excess of $N/10$-sodium hydroxide is then added, the solution boiled to expel ammonia, and titrated back with $N/10$-hydrochloric acid. From these data two values for the cyanate can be calculated, which serve to check one another (Chem. News, 1906, 93, 5; compare Zeitsch. angew. Chem. 1901, 24, 585; J. Soc. Chem. Ind. 1904, 23, 244).

$$KCNO+2HCl+H_2O = KCl+NH_4Cl+CO_2.$$

CYANIDES. (*a*) *By precipitation.* (i.) Excess of $N/10$-silver nitrate is added to the neutral cyanide solution, and then a little nitric acid. The excess of silver is titrated with $N/10$-thiocyanate after filtering off the silver cyanide. (ii.) The slightly alkaline solution is titrated with $N/10$-silver nitrate with constant stirring till a permanent turbidity is produced (Liebig, Annalen, 1851, 77, 102). This marks the end of the reaction:

$$2KCN+AgNO_3=KNO_3+KAg(CN)_2.$$

The end-point is best observed by adding 5–10 drops of 20 p.c. potassium iodide as an indicator. A permanent yellow turbidity, due to silver iodide, is produced as soon as the above reaction is completed (Ann. Chim. Phys. 1895, (vii.) 6, 381).

(*b*) See *Ferrocyanides* (*b*).

FERRICYANIDES. (*a*) The salt is reduced to ferrocyanide by boiling with sodium hydroxide and ferrous sulphate and the filtered solution strongly acidified with sulphuric acid and titrated with $N/10$-permanganate (*v. Ferrocyanides*). Reduction may also be effected by boiling with sodium peroxide (Arch. Pharm. 232, 226).

(*b*) *Iodimetrically.* The neutral solution (50 c.c.) is mixed with 3 grams of potassium iodide and 1·5 grams of zinc sulphate, the mixture well shaken, and the iodine titrated with $N/10$-thiosulphate. $2K_3Fe(CN)_6=I_2$ (Zeitsch. anorg. Chem. 1910, 67, 418; compare *ibid.* 67, 322).

FERROCYANIDES. (*a*) *By oxidation.* The solution is strongly acidified with sulphuric acid and titrated with $N/10$-permanganate till the colour changes from yellowish-green to yellowish-red. If any difficulty is experienced in determining the end-point, a drop of the solution may be mixed with dilute ferric chloride. A blue colour will develop whilst any ferrocyanide remains (de Haen, Annalen, 1854, 90, 160; compare Zeitsch. anorg. Chem. 1910, 67, 418).

An excess of permanganate may also be added, the excess being determined iodimetrically. (For details, consult Zeitsch. anorg. Chem. 1910, 67, 322.)

(*b*) *By conversion into hydrocyanic acid.* The ferrocyanide solution is boiled for five minutes with 10 c.c. of N-sodium hydroxide and 15 c.c. of $3N$-magnesium chloride, 100 c.c. of boiling $N/10$-mercuric chloride are then added, and the boiling continued for ten minutes. The mercuric cyanide produced is distilled for thirty minutes with 30 c.c. of $3N$-sulphuric acid, the prussic acid collected in 25 c.c. of N-sodium hydroxide, a little potassium iodide added, and the cyanide titrated with $N/10$-silver nitrate (Feld, Chem. Zentr. 1903, ii. 1398; Analyst, 1908, 33, 261; 1910, 35, 295).

THIOCYANATES. (*a*) *By precipitation.* As in standardising ammonium thiocyanate solution; the thiocyanate must be added to the silver nitrate, and not *vice versâ*, since nitric acid decomposes thiocyanates.

(*b*) *By oxidation.* The thiocyanate is titrated in concentrated hydrochloric acid solution with potassium iodate, in a stoppered bottle, with vigorous shaking. The end-point is reached when 5 c.c. of chloroform previously introduced are no longer coloured by iodine (J. Amer. Chem. Soc. 1908, 30, 760); *e.g.*

$$4CuCNS+7KIO_3+14HCl$$
$$=4CuSO_4+7KCl+7ICl+4HCl+5H_2O.$$

Oxidation in dilute sulphuric acid solution with permanganate is untrustworthy.

Cerium. (*a*) *Iodimetrically.* Ceric oxide is warmed with concentrated hydrochloric acid and potassium iodide in a stoppered bottle till complete solution is effected. The liberated iodine is then titrated with $N/10$-thiosulphate (Bunsen, Annalen, 1858, 105, 49; also Amer. J. Sci. 1899, 8, 451).

$$2CeO_2+8HCl+2KI=2CeCl_3+2KCl+I_2+4H_2O$$

(*b*) *By oxidation.* The washed oxalate is suspended in hot dilute sulphuric acid and titrated with $N/10$-permanganate (*v. Calcium;* Zeitsch. anal. Chem. 1880, 19, 194; Amer. J. Sci. 1899, 8, 457).

(*c*) *By reduction.* The cerium is oxidised with sodium bismuthate in boiling sulphuric acid solution to ceric sulphate and the filtered solution reduced by a slight excess of ferrous sulphate, the excess being titrated with *N*/10-permanganate. Other rare earth metals do not interfere (J. Amer. Chem. Soc. 1909, 31, 523; 1910, 32, 642; compare Compt. rend. 1899, 128, 101; Ber. 1900, 33, 1924; Ber. 1903, 36, 282).

(*d*) *Other methods* (Zeitsch. anorg. Chem. 1907, 54, 104; 1908, 59, 71).

Chlorine *v. Halogens.*

Chromium. The chromium should be in the form of chromate.

(*a*) *Iodimetrically.* The chromate solution is acidified with hydrochloric acid (5 c.c. of concentrated acid per 100 c.c. solution), 1 or 2 grams of potassium iodide added, and the covered solution allowed to stand for 15 to 20 minutes. It is then diluted to 400–500 c.c. and the liberated iodine titrated with *N*/10-thiosulphate. $3I_2=2Cr$. A known dichromate solution can in this way be used to standardise sodium thiosulphate (J. pr. Chem. 1868, 103, 362; Zeitsch. anorg. Chem. 1899, 19, 427; 1906, 49, 277; Zeitsch. angew. Chem. 1900, 1147).

(*b*) *By reduction* (i.) with ferrous ammonium sulphate, of which a slight excess is added to the chromate solution containing sulphuric or hydrochloric acid, the excess of ferrous salt being then titrated with *N*/10-dichromate; (ii.) with titanous chloride (*v. Preparation of standard solutions*; J. Soc. Chem. Ind. 1908, 27, 673); (iii.) with arsenious oxide (Amer. J. Sci. 1896, 1, 35).

Chromium in chrome steel. Three grams of alloy are dissolved in 35 c.c. of concentrated hydrochloric acid, and the excess evaporated; 150 c.c. of strong nitric acid are added, the boiling continued till no more brown fumes are evolved, when all chlorine has been expelled. The chromium is then oxidised by adding 10 grams of potassium chlorate, and the solution boiled down to 40 c.c. to decompose excess of chlorate; 100 c.c. of water are added, and one or two drops of hydrochloric acid, to dissolve separated manganese dioxide. The chromate solution is boiled to expel chlorine, cooled and titrated according to method (*b*) (i.) above. (For other methods, *see* J. Amer. Chem. Soc. 1905, 27, 1550; 1908, 30, 1116; J. Soc. Chem. Ind. 1907, 26, 1010; Chem. News, 1904, 90, 320; 91, 3; also *Manganese* and *Vanadium* (*v. infra*).)

Chromium in chromite. The valuation of this, the only important ore of chromium, is usually effected by a volumetric method; the finely powdered ore is fused with sodium peroxide in a nickel crucible, and the chromate in the aqueous extract estimated as described above, after boiling for ten minutes to decompose excess of peroxide (*v.* J. Soc. Chem. Ind. 1896, 15, 155, 436; Chem. Zeit. 1897, 21, 3; Bull. Soc. Chim. 1909, 5, 1133; Chem. News, 1896, 73, 1).

Cobalt. (*a*) *Iodimetrically.* The solution is mixed with hydrogen peroxide, and then with sodium hydroxide, when the cobalt is precipitated as sesquioxide Co_2O_3, whilst nickel is simply precipitated as green hydroxide. After boiling for a minute, the black ppt. is dissolved in hydrochloric acid and potassium iodide, and the iodine titrated with *N*/10-thiosulphate (Chem. News, 1900, 82, 66, 73; 1903, 88, 184).

(*b*) *By precipitation* with ferrocyanide, as described under *Nickel* (*b*).

Columbium. *By reduction and subsequent oxidation* (*v.* Zeitsch. anorg. Chem. 1909, 62, 383).

Copper. (*a*) *Iodimetrically.* The solution of cupric salt preferably neutral or containing acetic acid, is diluted to 100 c.c., 5 grams of potassium iodide are added, and the liberated iodine titrated with *N*/10-thiosulphate, using starch paste as indicator. If more than 25 c.c. of thiosulphate are required, 2–3 grams more potassium iodide should be added (Amer. J. Sci. 1907, 24, 65; compare J. Amer. Chem. Soc. 1902, 24, 1082; 1905, 27, 1224; see also *Methods of separation*).

$$2CuSO_4+4KI=2K_2SO_4+I_2+Cu_2I_2.$$

(*b*) *By titration with potassium cyanide* (*Steinbeck's process*). The ammoniacal copper solution is titrated with potassium cyanide until colourless (*v.* Chem. News, 1897, 76, 189; *Methods of separation*; and the article Copper).

(*c*) *By precipitation as thiocyanate* and estimation of the precipitate by potassium iodate in hydrochloric acid solution (*v. Thiocyanates*; and J. Amer. Chem. Soc. 1908, 30, 760).

(*d*) *By oxidation.* The oxalate is precipitated in a nitric acid solution by adding excess of ammonium oxalate, washed and titrated with *N*/10-permanganate (Amer. J. Sci. 1909, 27, 448).

(*e*) *By reduction* to cuprous salt. To the sulphuric or hydrochloric acid solution, 10–20 c.c. of 10 p.c. potassium thiocyanate and a little ferrous salt are added, when a deep red colouration is produced, since ferrous salts in acid solution are partly oxidised by cupric salts. The cold solution is titrated with titanous chloride until the red colouration is destroyed (Chem. Soc. Trans. 1906, 89, 1491). Or a slight excess of titanous chloride may be added, and titrated back with standard ferric alum.

Fluorine. *Acidimetrically.* The fluoride is mixed with ten times its weight of finely powdered and ignited quartz, and decomposed by warming with concentrated sulphuric acid; the silicon fluoride evolved passes through a dry U-tube filled with glass beads and immersed in cold water, in order to remove sulphuric acid, and is then absorbed in 50 p.c. alcoholic potassium chloride, which precipitates silicic acid and potassium silicofluoride, leaving hydrochloric acid in the solution:—

$$3SiF_4+2H_2O=2H_2SiF_6+SiO_2$$
$$H_2SiF_6+2KCl=K_2SiF_6+2HCl.$$

The hydrochloric acid is titrated with *N*/5-sodium hydroxide, using lacmoid as indicator. $2HCl=3F_2$. (For full experimental details, which are absolutely essential in order to obtain accurate results, consult Chem. News, 1879, 39, 179; Amer. J. Sci. 1906, 22, 329; or Low's Technical Methods of Ore Analysis.)

Gold. *Iodimetrically.* The auric solution is treated with potassium iodide in more than sufficient quantity to dissolve the aurous iodide first precipitated, and the iodine liberated is estimated with standard thiosulphate (Amer. J. Sci. 1899, 8, 261; compare Zeitsch. anorg. Chem. 1899, 19, 63).

Halogens. This term is restricted in this connection to chlorine, bromine, and iodine, fluorine being treated separately, since its analytical reactions are quite different.

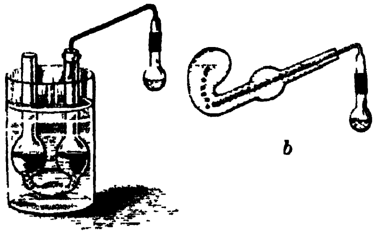


Fig. 13.

Estimation of halogens. *Iodine* is estimated by solution in potassium iodide and titration with $N/10$-thiosulphate, using starch paste as indicator (*v. Preparation of standard solutions*, *Bromine* and *chlorine* are absorbed in potassium iodide solution, setting free an equivalent quantity of iodine, which is titrated with $N/10$-thiosulphate.

A large number of substances, *e.g.* peroxides, chlorates, chromates, &c., may be readily determined indirectly by distillation with concentrated hydrochloric acid, the available oxygen of the compound setting free its equivalent of chlorine, which is absorbed in potassium iodide, and the liberated iodine titrated with $N/10$-thiosulphate. It is very desirable to exclude air in the process of distillation, since it liberates iodine from the hydrogen iodide set free in the receiver, by the hydrogen chloride distilling over during the experiment. The apparatus devised by Bunsen, the originator of this analytical method, is shown in Fig. 13, *b*. The small flask (50 c.c.) and the delivery tube are ground at their junction to fit, and the joint made with caoutchouc tubing; a ground-glass joint is better, a spring holding the two parts tightly together. The mixture is rapidly boiled, the chlorine passing into potassium iodide contained in the retort, the size of which must be suitably chosen to prevent overflowing. A different receiving vessel is shown in Fig. 13, *a*. It is very convenient to perform such distillations in a current of carbon dioxide or other inert gas, and various designs of apparatus for such a purpose are given in Amer. J. Sci. 1898, 6, 168; Chem. News, 1899, 79, 85; Chem. Soc. Trans. 1892, 61, 87; Zeitsch. angew. Chem. 1890, 477.

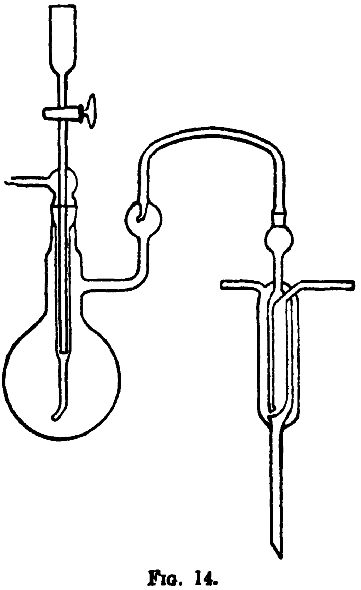


Fig. 14.

The apparatus shown in Fig. 14 (Analyst, 1908, 33, 117) admits of the gradual introduction of a liquid reagent during distillation in carbon dioxide, steam, or any other gas or vapour. Contamination of the reagents with cork or indiarubber derived from stoppers, &c., is avoided by fitting the condenser and the dropping funnel to the distilling flask by ground-glass joints.

Estimation of halogens in halide salts. *By precipitation.* (i.) *Mohr's method.* The neutral solution is titrated with $N/10$-silver nitrate in the presence of a few drops of potassium chromate as indicator (*v. Preparation of standard solutions*. It is advisable to perform a blank experiment under identical conditions, to allow for the silver nitrate necessary to bring out the reddish colouration. (ii.) *Volhard's method.* The nitric acid solution of the halide is precipitated by adding a slight excess of $N/10$-silver nitrate, the excess being then titrated with $N/10$-ammonium thiocyanate. Silver chloride must be filtered off before the latter titration is performed, since it reacts with the thiocyanate (J. Amer. Chem. Soc. 1907, 29, 269; compare Zeitsch. anorg. Chem. 1909, 63, 330); but silver bromide and iodide do not interfere. It is advisable to titrate iodide in a stoppered bottle with vigorous shaking when adding both the silver solution and the thiocyanate, to minimise error due to occlusion. It is more accurate to weigh out a very slight excess of pure silver, dissolve it in nitric acid (carefully expelling nitrous acid, which interferes with the indicator), and add to the halide solution than to measure out $N/10$-silver nitrate. After vigorous shaking, the excess of silver is then titrated with a dilute thiocyanate solution (1 c.c. = 1 milligram Ag).

Iodides. *Iodimetrically.* (i.) A slight excess of potassium iodate is added, and the solution acidified with dilute sulphuric acid. The liberated iodine is extracted with chloroform, carbon disulphide or toluene, and titrated with $N/10$-thiosulphate. A weaker acid than sulphuric acid may be employed, *e.g.* acetic or tartaric acid. Five-sixths of the iodine found was originally present as iodide (Chem. Zeit. 1904, 28, 1191; Amer. J. Sci. 1897, 3, 293; J. pharm. Chim. 1902, 16, 207; J. Amer. Chem. Soc. 1903, 25, 1138). This method is available in the presence of bromide and chloride, if acetic acid be employed. (ii.) The solution, containing the iodide, 2 grams of pure potassium arsenate, and 10 c.c. of concentrated sulphuric acid, is boiled down from a volume of 100 c.c. to

35-40 c.c., when all the iodine is expelled. The arsenious salt in solution is then titrated with $N/10$-iodine (Amer. J. Sci. 1890, 39, 188). $As = I_2$. In the presence of chloride the results are a little low; bromide causes them to be slightly high. (iii.) (*v.* Chem. Soc. Trans. 1885, 47, 471.)

ESTIMATIONS OF HALOGENS IN OXYHALOGEN COMPOUNDS. (*a*) *By reduction* to a halide salt and determination of the latter. *Iodates* are reduced by adding sulphurous acid to the sulphuric acid solution of the iodate till the separated iodine is redissolved; an excess of $N/10$-silver nitrate is added to precipitate the iodide, the mixture boiled with excess of nitric acid, and finally the excess of silver titrated with $N/10$-thiocyanate. *Bromates and chlorates* are reduced by adding an excess of iron filings to the sulphuric acid solution; after an hour, excess of $N/10$-silver nitrate is added, the mixture boiled with nitric acid to oxidise the ferrous salt, and the excess of silver titrated (Amer. Chem. J. 1904, 32, 242).

(*b*) *By reduction* to a halide salt and estimation of the reducing agent used up in the process. With *chlorates and bromates*, the sulphuric acid solution is boiled for ten minutes with excess of standard ferrous sulphate in an atmosphere of carbon dioxide, the solution cooled, manganese sulphate added and the unchanged ferrous salt titrated with $N/10$-$KMnO_4$. $6Fe = ClO_3$ or BrO_3 (Zeitsch. anorg. Chem. 1904, 38, 110). *Bromates* may also be reduced with arsenious oxide (Amer. J. Sci. 1902, 14, 285). *Chlorates* are reduced by adding an excess of $N/10$-titanous sulphate, and after three minutes, titrating back with ferric alum (J. Soc. Chem. Ind. 1908, 27, 434).

(*c*) *Iodimetrically. Chlorates.* (i.) By distillation with concentrated hydrochloric acid. $ClO_3 = 3I_2$ (*Bunsen's method; v. Estimation of halogens;* Chem. Soc. Trans. 1892, 61, 87). (ii.) By reduction with concentrated hydrochloric acid and potassium bromide (Chem. Zeit. 1901, 25, 727), or with potassium iodide and dilute sulphuric acid in presence of vanadyl sulphate (Zeitsch. anal. Chem. 1907, 46, 521). (For other methods, *see* Amer. J. Sci. 1891, 42, 220; J. Amer. Chem. Soc. 1903, 25, 756; Zeitsch. anal. Chem. 1907, 46, 308.)

Hypochlorites. A slight excess of $N/10$-sodium arsenite is added and the excess titrated with $N/10$-iodine, or the hypochlorite is directly titrated with the arsenite till a drop of the solution ceases to colour starch-potassium iodide paper blue. $As = ClO$ (*Penot's method*; compare Chem. Zeit. 1904, 28, 59).

Perchlorates. The concentrated solution is boiled with a large excess of titanous sulphate, the excess oxidised with permanganate, and the chloride produced is titrated as usual (Zeitsch. anorg. Chem. 1909, 62, 108; Chem. Zeit. 1909, 33, 759).

Bromates. The substance is digested at 100° with potassium iodide and concentrated hydrochloric acid in a stoppered bottle, and the liberated iodine titrated with thiosulphate. $BrO_3 = 3I_2$ (compare Zeitsch. anorg. Chem. 1899, 19, 427).

Iodates. These are simply added to a slight excess of potassium iodide solution, acidified with sulphuric or hydrochloric acid, and the liberated iodine titrated. $IO_3 = 3I_2$.

ESTIMATIONS INVOLVING MIXTURES OF THE FOREGOING HALIDE SALTS.

Chloride, Hypochlorite and Chlorate. The solution is titrated with $N/10$-sodium arsenite by Penot's method for the *hypochlorite*; the *chlorate* is then estimated in the solution, after acidifying with sulphuric acid, by reduction with standard ferrous sulphate, and the total chlorine then titrated by Volhard's method (Compt. rend. 1896, 122, 449; cf. J. Amer. Chem. Soc. 1909, 31, 525, 1273).

Chloride, Chlorate and Perchlorate. Chloride is titrated in one portion of the solution by Volhard's method, and in another portion after reducing the chlorate with ferrous sulphate. For *perchlorate* the dry substance, mixed with five times its weight of pure quartz sand and covered with a layer of the same 2 cm. deep, is fused in a platinum crucible for half an hour, cooled, extracted with water, and the total chloride estimated (Compt. rend. 1896, 122, 452).

Chloride and Iodide. The *total halogen* is titrated by a suitable method in one portion of solution, and the *chlorine* in another portion after removing iodine by one of the following methods (Amer. J. Sci. 1890, 39, 293). (i.) To the neutral solution (400 c.c.) is added 10 c.c. sulphuric acid (1 : 1), 2 grams ferric sulphate, and 3 c.c. nitric acid, and the whole boiled till all iodine is expelled; 1 c.c. nitric acid is again added, and the solution again boiled. (ii.) The ferric sulphate and nitric acid of method (i.) are replaced by 2 grams of pure sodium nitrite (or, failing this, by passing into the solution the vapours generated from the slightly impure nitrite and dilute sulphuric acid).

Bromide and Iodide (*v. supra, Iodides*).

Bromide and Chloride. The solution is acidified so as to contain 25 c.c. of concentrated nitric acid in a total volume of 100 c.c., heated to boiling and boiled for one minute, the source of heat removed and air sucked through the solution until it is perfectly colourless (and for one minute longer). The bromine is then completely expelled; the residual *chloride* is titrated by Volhard's method. The *total halogens* are titrated in another portion of solution (J. Soc. Chem. Ind. 1909, 28, 505).

(For a very accurate but more elaborate method, *v.* J. Amer. Chem. Soc. 1907, 29, 275; also Zeitsch. anorg. Chem. 1895, 10, 387; Zeitsch. anal. Chem. 1900, 39, 81.)

Chloride, Bromide, and Iodide. (*a*) The *iodide* is decomposed with potassium iodate and acetic acid, the iodide extracted with chloroform and titrated. The *bromide* is destroyed by boiling with $5N$-nitric acid, any iodate remaining is decomposed with a slight excess of potassium iodide, which excess is readily decomposed by boiling with nitric acid, and the residual *chloride* titrated. The total *halogens* are titrated in another portion of solution (J. Amer. Chem. Soc. 1903, 25, 1138).

(*b*) The *iodide* is destroyed by boiling with ferric sulphate and sulphuric acid, and the amount of ferric salt reduced is determined with $N/10$-dichromate. The *total halogens* are determined by Volhard's method, and, in another portion of solution, the iodide is removed by adding hydrogen peroxide and acetic acid and distilling in steam, the bromine separated as described under *Bromide and Chloride* and the residual *chloride* titrated (J. Soc. Chem. Ind. 1909, 28, 505).

Iron. FERROUS SALTS. *By oxidation.* (a) The cold solution is strongly acidified with dilute sulphuric acid and titrated with $N/10$-permanganate. This simple and accurate method requires modification when hydrochloric acid is present, since it reacts with permanganate. This side-reaction can be practically prevented by adding a moderate quantity of manganese sulphate to the solution and titrating very slowly. A solution is prepared as follows: 67 grams of crystalline manganese sulphate are dissolved in water, 138 c.c. of phosphoric acid (sp.gr. 1·7), and 130 c.c. concentrated sulphuric acid (sp.gr. 1·82) are added, and the mixture diluted to 1 litre. Of this solution, 25 c.c. are added to the ferrous solution to be titrated. The phosphoric acid keeps the ferric solution colourless, and thus facilitates the observation of the end-point (Zeitsch. anal. Chem. 1863, 1, 329; Chem. Zeit. 1889, 13, 323; Amer. Chem. J. 1905, 34, 109; Analyst, 1908, 33, 43, and 1909, 34, 306).

(b) The acid solution is oxidised by $N/10$-dichromate as described under *Preparation of standard solutions.*

FERRIC SALTS. (a) *By reduction* to ferrous salt and titration with permanganate or dichromate. Reduction may be effected in any of the following ways: (i.) The sulphuric acid solution is heated to boiling and hydrogen sulphide passed through it until the solution is completely colourless; the excess of hydrogen sulphide is expelled from the boiling solution by a current of carbon dioxide. (ii.) The nearly neutral solution is boiled with sulphurous acid or ammonium sulphite, excess being removed by continued boiling, preferably in a current of carbon dioxide. (iii.) Eight or ten grams of granulated zinc are added to the warm sulphuric acid solution, and the action allowed to continue until a drop of the solution no longer gives a colouration with potassium thiocyanate. The solution is cooled, filtered through glass wool, and titrated. The use of the zinc-copper couple is preferable (Analyst, 1901, 26, 225; compare Chem. News, 1908, 97, 50). Reduction may be rapidly effected by pouring the liquid through a long column of zinc (The Jones' Reductor (Fig. 15); Chem. News, 1889, 60, 93; Blair's Chemical Analysis of Iron, 6th ed. 94). (iv.) The hydrochloric acid solution is heated nearly to boiling, and stannous chloride (25 p.c. solution) added drop by drop until the solution is colourless; 10 c.c. of saturated mercuric chloride are added to destroy excess of stannous chloride, the solution diluted, manganese sulphate added (*v. supra*), and the ferrous salt titrated with $N/10$-permanganate [best after the addition of about 5 c.c. of water-glass solution of sp.gr. 1·17] (Analyst, 1909, 34, 306). (v.) *Reduction by palladium-hydrogen* in boiling acid solution; this introduces no foreign substance into the solution (Zeitsch. angew. Chem. 1902, 15, 398, 424; Analyst, 1904, 29, 346). (vi.) *Reduction with titanous sulphate* (Amer. J. Sci. 1908, 25, 343).

(b) *By direct titration with a reducing agent.* (i.) *Titanous chloride.* The sulphuric or hydrochloric acid solution of the ferric salt is titrated as described under *Preparation of standard solutions.* (ii.) *Stannous chloride.* The nearly boiling hydrochloric solution is titrated as described under *Preparation of standard solutions*, using either the mercuric chloride indicator (Amer. Chem. J. 1893, 15, 360) or titrating back with iodine.

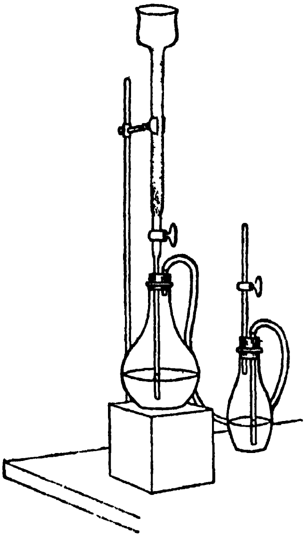


FIG. 15.

FERROUS IRON IN MINERALS AND ROCKS. The only satisfactory method consists in decomposing the coarsely powdered substance with sulphuric and hydrofluoric acids in an atmosphere of carbon dioxide, and titrating the ferrous salt produced (*Cooke's Method*; Amer. J. Sci. 1867, 44, 347; *see* also Amer. J. Sci. 1894, 48, 149). The old method of heating with dilute sulphuric acid in a sealed tube (Mitscherlich) is worthless in the presence of sulphur or sulphides (J. Amer. Chem. Soc. 1900, 22, 625). (For an exhaustive discussion of this problem, *v.* Hillebrand's Analysis of Silicate and Carbonate Rocks.)

Iron and Aluminium. After weighing the ignited sesquioxides, they are brought into solution by fusion with potassium hydrogen sulphate or acid potassium fluoride (followed by evaporation with sulphuric acid), and the *iron* reduced and titrated (Zeitsch. angew. Chem. 1905, 18, 815).

Iron and Titanium. Ferric salts can be reduced with sulphurous acid or hydrogen sulphide without reducing *titanic* salts; or reduction of both may be effected with zinc and sulphuric acid, the *titanous* salt oxidised with a slight excess of bismuth oxide, and the *ferrous* salt titrated in the filtered solution. To estimate both elements present, one of the preceding methods may be combined with the reduction process for titanium, described later, which would give the *total iron and titanium* (*v.* also J. Soc. Chem. Ind. 1909, 28, 189; Analyst, 1910, 35, 198).

Iron and Vanadium. Reduction with sulphur dioxide proceeds with the vanadium as far as to the oxide V_2O_4; reduction with zinc carries it as far as V_2O_2; hence two such reductions and titrations with permanganate furnish data for calculating both iron and vanadium (Amer. J. Sci. 1908, 26, 79).

Lead. *By precipitation* (i.) *As molybdate.* The boiling acetic acid solution is titrated with standard ammonium molybdate (4·75 grams per litre, titrated against pure lead) until a drop of solution gives a brown or yellow colour with a drop of dilute tannic acid solution. The indicator not being very sensitive, a 'blank' experiment should be made and the necessary correction allowed for both in an assay and in standardising the solution. (ii.) *As ferrocyanide.* The cold acetic acid solution is titrated with potassium ferrocyanide (10 grams per litre titrated against pure lead) until a drop of the solution produces a brown colouration with a drop of saturated uranium acetate solution; a 'blank' experiment should also be made (J. Amer. Chem. Soc. 15, 550; Chem. News, 1896, 73, 18). In determining lead in ores, &c., it is usually separated as sulphate and dissolved in ammonium acetate previous to titration. (For a comprehensive review of methods for lead, *v.* Chem. News, 1903, 87, 40; Gaz. chim. ital. 1896, 26, i. 327; *see* also *Methods of separation*; and J. Amer. Chem. Soc. 1903, 25, 632; 1904, 26, 1135.)

Magnesium. (*a*) *Acidimetrically.* The magnesium is precipitated as the double ammonium phosphate, the precipitate washed with dilute ammonia, and then with aqueous alcohol till free from extraneous ammonia, dissolved in a measured excess of *N*/10-hydrochloric acid, and the excess titrated with *N*/10-sodium hydroxide, using methyl orange for indicator:

$$Mg(NH_4)PO_4+2HCl = MgCl_2+H_2(NH_4)PO_4$$

(Chem. Zentr. 1876, 727; for a method which obviates the use of alcohol, *v.* J. Amer. Chem. Soc. 1900, 22, 31; *see* also *Phosphorus*).

(*b*) *Iodimetrically.* The magnesium is precipitated as double ammonium arsenate, dissolved in hydrochloric acid and potassium iodide, and the iodine titrated (J. Amer. Chem. Soc. 1899, 21, 746; Zeitsch. anal. Chem. 1907, 46, 714).

Manganese. (*a*) *By oxidation with permanganate.* (*Volhard's method, modified.*) The neutral chloride or sulphate solution containing 10 grams of zinc sulphate is heated to boiling, 1 gram of freshly ignited zinc oxide added, and the liquid titrated with *N*/10-permanganate, boiling and shaking frequently until the supernatant liquid is red; 1 c.c. pure glacial acetic acid is added, and the titration slowly finished with permanganate in the hot *but not boiling* liquid. The manganese can be accurately calculated from the equation:

$$3MnO+Mn_2O_7 = 5MnO_2$$

(Zeitsch. anal. Chem. 1909, 48, 751; Little and Cahen, Analyst, 1911, 36, 52).

(*b*) *By precipitation as dioxide* and estimation of the available oxygen. Precipitation may be effected in one of the following ways: (i.) By adding bleaching-powder solution and calcium carbonate to a hot, neutral solution of the manganese salt containing ferric and zinc chlorides (Chem. Soc. Trans. 1879, 35, 365; J. Soc. Chem. Ind. 1891, 10, 333). (ii.) By boiling the solution in concentrated nitric acid (quite free from any hydrochloric acid) with potassium (or preferably sodium) chlorate. (iii.) By boiling the dilute sulphuric acid solution with ammonium persulphate (Zeitsch. angew. Chem. 1901, 14, 1149; 1903, 16, 905; Compt. rend. 1902, 135, 965; 1903, 136, 449). The washed precipitate in either case is dissolved in a sulphuric acid solution of standard ferrous sulphate or oxalic acid, and the excess of reagent titrated. The precipitate obtained by method (ii.) is deficient in available oxygen (Amer. J. Sci. 1898, 5, 260), and the standard solution employed in the final titration must therefore be standardised on a known amount of manganese treated in a similar fashion.

(*c*) *By conversion into permanganic acid.* (i.) The cold solution free from hydrochloric acid, and containing one quarter its volume of nitric acid (specific gravity 1·42), is oxidised by shaking with 2–4 grams of sodium bismuthate for three minutes, diluted with half its volume of 3 p.c. nitric acid, the solid residue allowed to settle, and the permanganic acid solution filtered into a slight excess of ferrous sulphate; excess of the latter is then titrated with *N*/10-permanganate (Dingl. poly. J. 269, 224; Chem. Soc. Trans. 1895, 67, 268; Chem. News, 1901, 84, 209, 247; J. Amer. Chem. Soc. 1904, 26, 793). (ii.) The oxidation of small quantities of manganese may be effected by boiling the nitric acid solution with lead peroxide, or by heating with ammonium persulphate in the presence of a little silver nitrate (Chem. News, 1901, 84, 239).

Manganese in Ferromanganese and Steels. The foregoing methods *a*, *b*, and *c* (i.) have all been employed for this purpose; method *c* (i.) is the simplest and probably the most accurate. In method *a* it is necessary to remove iron from the solution; this is conveniently performed by adding a slight excess of zinc oxide to the solution (*v.* references given above; also J. Amer. Chem. Soc. 1902, 24, 243; Ann. Chim. anal. 1906, 11, 124).

Manganese and Chromium occurring together in steels may be estimated by oxidising with ammonium persulphate in sulphuric acid solution in the presence of silver nitrate; one portion of solution is titrated for total permanganate and chromate with ferrous sulphate, and another for permanganate alone by means of arsenious oxide (J. Amer. Chem. Soc. 1905, 27, 1550; *v.* also Chem. News, 1901, 83, 25; 1905, 91, 3; Chem. Zeit. 1905, 29, 987; Chem. Zeit. Rep. 1905, 29, 380).

The foregoing bismuthate method *c* (i.) may be applied in the presence of *molybdenum, tungsten, titanium*, and *vanadium*; also, with certain precautions, in the presence of *chromium* (Chem. News, 1901, 84, 247). (For estimating *manganese* in *tungsten steels*, *v.* also J. Soc. Chem. Ind. 1907, 26, 345.)

Mercury. (*a*) *By precipitation.* Mercuric nitrate is readily titrated with *N*/10-thiocyanate, using ferric nitrate as indicator, provided that nitric acid is present in fairly high concentration (Ber. 1901, 34, 3502; 1902, 35, 2015). Chloride must be absent; if necessary, the mercury is precipitated as oxide with sodium hydroxide, and the washed precipitate dissolved in nitric acid.

(*b*) *Iodimetrically.* The mercuric solution (25–50 c.c.) containing 1 gram of potassium iodide is made alkaline with sodium hydroxide, 2–3 c.c. of 40 p.c. formaldehyde added, and the whole shaken vigorously for two minutes. The solution is acidified with acetic acid, and the reduced mercury is dissolved by adding an excess of *N*/10-iodine. After shaking, the excess of iodine above that required to form mercuric iodide is titrated with *N*/10-thiosulphate (Ber. 1906, 39, 3702; 1907, 40, 3276; Bull. Soc. chim. 1907, [iv.] 1, 1169). Mercurous salts require a preliminary oxidation.

(For other methods, *v.* Compt. rend. 1863, 56, 63; Chem. Soc. Trans. 1892, 61, 364; Arch. Pharm. 241, 444.)

Molybdenum. (*a*) *By reduction and subsequent oxidation.* The sulphuric acid solution is reduced by passing it through a long column of amalgamated zinc to a condition represented by the formula Mo_2O_3; the liquid is caught directly in ferric sulphate solution, which reoxidises the molybdenum salt, and the ferrous sulphate produced is titrated with *N*/10-permanganate (Amer. J. Sci. 1907, 24, 313; compare Ber. 1905, 38, 604; Analyst, 1907, 32, 250).

(*b*) *Iodimetrically.* The solution in concentrated hydrochloric acid is boiled with a slight excess of potassium iodide till the volume is reduced to 25 c.c., when complete reduction to the condition Mo_2O_5 is effected. The solution is cooled, diluted to 125 c.c., 0·5 gram of manganese sulphate added, and then a slight excess of *N*/10-permanganate; *N*/10-arsenious acid is next added, and after the addition of tartaric acid and sodium bicarbonate, the excess is titrated with *N*/10-iodine. The permanganate *plus* iodine and *minus* the arsenious acid measure the Mo_2O_5 present (Amer. J. Sci. 1901, 12, 449; compare *ibid.* 1896, 2, 156; 1898, 6, 168).

Molybdenum in Steels and Alloys (*v.* J. Amer. Chem. Soc. 1904, 26, 675).

Nickel. (*a*) *By double cyanide formation.* A few drops of 10 p.c. potassium iodide are added to the cold, slightly ammoniacal nickel solution, and then a small measured volume of silver nitrate (3 grams of silver per litre). Standard potassium cyanide (25 grams per litre) is then run in with stirring till the precipitate of silver iodide just disappears; more silver nitrate is added till a very faint turbidity is produced, which is then dissolved by the least possible excess of cyanide. The relative values of the silver nitrate and cyanide solutions are determined by a preliminary experiment, and the cyanide standardised against a known amount of pure nickel (or pure silver, and calculated to nickel). The method is rapid and accurate (Chem. News, 1895, 72, 92).

(*b*) *By precipitation.* The hot nickel solution containing ferric chloride and citric acid is made feebly ammoniacal and titrated slowly, stirring constantly, with standard potassium ferrocyanide (20 grams per litre, titrated against pure nickel), until a drop of the solution when acidified with dilute acetic acid develops a green colour in five minutes (J. Amer. Chem. Soc. 1910, 32, 757; Bull. Soc. chim. 1907, 4, 1163).

Nickel in Steel. Method (*b*) can be directly applied; method (*a*) can also be employed without removing iron, molybdenum, or chromium, if a sufficient excess of ammonium citrate or sodium pyrophosphate is added to the solution; or a moderate amount (2–3 grams) of each of these reagents may be added (J. Amer. Chem. Soc. 1907, 29, 1201; 1908, 30, 1116; 1899, 21, 854; Chem. Zeit. 1908, 32, 1223). (For modifications in presence of other metals, *v.* Chem. News, 1898, 78, 177, 190.)

Nitrogen. AMMONIA (*v.* ACIDIMETRY AND ALKALIMETRY).

HYDRAZINE. *Iodimetrically.* A moderate excess of sodium bicarbonate or sodium acetate is added to the solution of a hydrazine salt, which is then titrated with *N*/10-iodine. $N_2H_4=2I$ (J. pr. Chem. 1902, 66, 332; 1903, 67, 140; *v.* also Gazz. chim. ital. 1899, 29, 265).

HYDROXYLAMINE. (*a*) *By oxidation.* The solution of a hydroxylamine salt is slowly added to excess of boiling and well-stirred Barreswil's (Fehling's) solution, the precipitated cuprous oxide washed, dissolved in acid ferric alum, and the ferrous salt titrated with permanganate. $NH_2OH=Cu_2$ (Chem. Soc. Trans. 1903, 83, 1394; compare Ber. 1877, 10, 1940).

(*b*) *By reduction.* An excess of titanium sesquisulphate is added to the acid solution, and the ammonium salt produced is estimated by distillation with sodium hydroxide (Ber. 1909, 42, 2695).

NITRATES. (*a*) *By reduction.* The solution is made strongly alkaline with sodium hydroxide, 5 c.c. of alcohol and 2·5–3 grams of powdered Devarda's alloy added, and the flask connected with a distilling apparatus, the receiver of which contains excess of *N*/2-hydrochloric acid. After standing for half an hour, the liquid is steam-distilled for an equal length of time, when all the nitrate has been converted into ammonia and driven over into the acid; the excess of the latter is then titrated (Zeitsch. anal. Chem. 1894, 33, 113; Analyst, 1910, 35, 307; *v.* also the *Gravimetric section*).

(*b*) *Iodimetrically* (*v.* Zeitsch. angew. Chem. 1890, 3, 477; Chem. Soc. Trans. 1891, 59, 530; Amer. J. Sci. 1892, 44, 117).

NITRITES. (*a*) *By oxidation.* The nitrite solution is slowly added to a measured quantity of *N*/10-permanganate, which is acidified with sulphuric acid, diluted to 400 c.c., and warmed to 40°, until the colour is just discharged. $2HNO_2 = O_2$. Otherwise, the cold dilute nitrite solution is slowly titrated with *N*/10-permanganate to a red colouration; a few drops of sulphuric acid are then added, followed by an excess of permanganate. The liquid is then strongly acidified with sulphuric acid, heated nearly to boiling, and the excess of permanganate titrated with *N*/10-oxalic acid (Amer. Chem. J. 1883, 5, 388).

(*b*) *Iodimetrically.* Several methods have been based on the reaction.

$$2HI+2HNO_2 = I_2+2NO+2H_2O.$$

It is necessary to perform the experiment in an atmosphere free from oxygen; the iodine may be determined by thiosulphate or arsenite. (For details, *v.* Pharm. J. 19, 741; Chem. News, 1904, 90, 114; *cf.* *Organic analysis,* Aromatic amines.)

Colorimetrically. Nitrous acid may be estimated by the formation of a yellow colour due to the production of paranitrosodimethylaniline, by adding a solution of dimethylaniline hydrochloride to an acidulated solution of the nitrous acid, and comparing the intensity of the colour produced with a standard solution of sodium nitrite with the same reagents. (For details, *see* Miller, Analyst, 1912, 37, 345.)

Osmium. *Iodimetrically* (*v.* Chem. Zentr. 1898, ii. 65).

Oxygen. PEROXIDES. (*a*) *Iodimetrically.* Such peroxides as those of manganese and lead may be estimated by distillation with concentrated hydrochloric acid, and collecting the chlorine evolved in potassium iodide (*Bunsen's method*). Finely divided peroxides of manganese react quantitatively with cold dilute hydrochloric acid and potassium iodide (Chem. Soc. Trans. 1880, 37, 128), a method of estimation that is available with the peroxides of the alkali and alkali earth metals, which do not give satisfactory results by the distillation method (Arch. Pharm. 1902, 240, 437). Hydrogen peroxide may be determined in this manner (Analyst, 1888, 13, 62).

(*b*) *By reduction.* Hydrogen peroxide, or peroxides of the alkali and alkaline-earth metals, may be dissolved in cold dilute acid and titrated with *N*/10-permanganate, which loses as much oxygen as is lost by the peroxide (*v.* also *Gas-Volumetric methods*).

(For critical reviews of methods, &c., *v.* Arch. Pharm. 228, 432; Amer. Chem. J. 1906, 36, 117; Zeitsch. angew. Chem. 1901, 14, 828; 1908, 21, 589; Chem. Zeit. 1906, 30, 1275; 1907, 31, 1257; Zeitsch. anal. Chem. 1908, 47, 465.)

Phosphorus. PHOSPHORIC ACID (ORTHO-). (*a*) (*v.* ACIDIMETRY AND ALKALIMETRY).

(*b*) *Acidimetrically, with previous precipitation.* (i.) The precipitated magnesium ammonium phosphate (*v. Gravimetric section*) is washed and titrated as described under *Magnesium* (Zeitsch. anal. Chem. 1898, 37, 217; Zeitsch. angew. Chem. 1905, 18, 655; compare Zeitsch. anal. Chem. 34, 33). (ii.) The precipitate of ammonium phosphomolybdate (*v. Gravimetric section*) after washing is dissolved in a slight excess of standard potassium hydroxide free from carbonate, and the excess titrated with standard nitric acid using phenolphthaleïn as indicator. One molecular proportion of P_2O_5 present as $(NH_4)_3PO_4,12MoO_3$, requires 23 molecules of K_2O in pure aqueous caustic potash. $P_2O_5{=}23K_2O$ (J. Amer. Chem. Soc. 1895, 17, 950; 1897, 19, 703; J. Soc. Chem. Ind. 1904, 23, 1186).

(*c*) *By precipitation.* To the solution, feebly acid with acetic acid, 10 c.c. of 10 p.c. ammonium acetate are added and standard uranium acetate solution (35 grams per litre) run in from a burette until a drop of the solution gives a brown colouration with potassium ferrocyanide upon a white tile. The solution is heated to boiling, when the latter reaction will no longer take place, and more uranium acetate added until the brown colouration is obtained once more, *e.g.*:

$$KH_2PO_4+UO_2(C_2H_3O_2)_2+NH_4{\cdot}C_2H_3O_2$$
$$= KC_2H_3O_2+2HC_2H_3O_2+UO_2NH_4PO_4$$

In analysing alkali phosphates, the uranium solution is standardised against pure potassium dihydrogen phosphate, while a solution of calcium phosphate in acetic acid, standardised gravimetrically by the method of Woy (Chem. Zeit. 1897, 21, 442), must be used if the uranium acetate is to be used for estimating phosphates of the alkaline earths (J. Soc. Chem. Ind. 1892, 11, 328). It is essential that titrations should be made under conditions closely approximating those which obtained when the uranium solution was standardised.

PHOSPHORUS IN IRON AND STEEL. This is usually separated as ammonium phosphomolybdate; it may then be titrated according to *b* (ii.) above, or the precipitate is washed with dilute ammonium sulphate, dissolved in ammonia, the solution strongly acidified with sulphuric acid, reduced with zinc, and the Mo_2O_3 solution collected directly in ferric alum, the ferrous salt being then titrated as described under *Molybdenum* (Amer. J. Sci. 1907, 24, 313; compare Blair's Analysis of Iron).

Potassium. *By oxidation.* The acetic acid solution, free from ammonium salts, is evaporated on the water-bath till pasty with sodium cobaltinitrite solution in rather large excess, cooled and stirred with 50–100 c.c. of cold water. The dipotassium sodium cobaltinitrite is collected, on asbestos, washed with cold water, and then immefsed in an excess of nearly boiling permanganate solution. After 5 minutes the solution is acidified with sulphuric acid, excess of *N*/10-oxalic acid added, and the clear solution titrated with permanganate. The permanganate is best standardised against a pure potassium salt. The oxidation of 2 molecular porportions of $K_2NaCo(NO_2)_6$ by permanganate requires 11 atomic proportions of oxygen or 4K = 22H (Amer. J. Sci 1907, 24, 433; compare Chem. Soc. Trans. 1900, 77, 1076). (For another method, *v.* Chem. Zeit. 1895, 19, 301.)

Selenium. SELENIOUS ACID. *By oxidation.* To the cold solution containing 5 p.c. by volume of concentrated sulphuric acid is added an excess of *N*/10-permanganate; a moderate excess of *N*/10-oxalic acid is then added, and the titration finished at 50°–60° with permanganate. $2SeO_2 = O_2$ (Amer. J. Sci. 1895, 50, 51).

(For an entirely different method, *v.* Amer. Chem. J. 1896, 18, 703; Amer. J. Sci. 1899, 7, 287.)

SELENIC ACID. *Iodimetrically.* (i.) The acid is boiled with hydrochloric acid (25 c.c. concentrated acid in a total volume of 75 c.c.) for 10 minutes in a Bunsen distilling apparatus or one of its various modifications, and the chlorine evolved is collected in potassium iodide (*v. supra, Volumetric estimation of halogens*, p. 209) $SeO_3 = Cl_2$ (Amer. J. Sci. 1895, 50, 400). (ii.) The solution (60 c.c.) containing 20 c.c. of sulphuric acid (1 : 1) and 1 gram of potassium bromide is distilled and the liberated bromine collected in potassium iodide. $SeO_3 = Br_2$ (Amer. J. Sci. 1895, 50, 402).

SELENIUM IN EITHER STATE OF OXIDATION. *Iodimetrically.* This is effected by a Bunsen distillation, the solution (60 c.c.) containing 5 c.c. of concentrated hydrochloric acid and 1–3 grams of potassium iodide. The selenium compound is reduced to the element itself, and an equivalent of iodine is distilled into potassium iodide and titrated. $SeO_2 = 2I_2$ and $SeO_3{=}3I_2$ (Amer. J. Sci. 1895, 50, 249; for a simpler method *v.* Amer. J. Sci. 1896, 1, 31).

Silver. *By precipitation.* (i.) The nitric acid solution is titrated with standard sodium chloride until no further precipitation is observed. (For details of this very exact method, *v.* the article on ASSAYING.) A number of devices have been described for rapidly filtering a portion of the liquid in order to test it for further precipitation (Chem. Soc. Trans. 1908, 93, 1037; Gazz. chim. ital. 1909, 39, ii. 240). A modified method consists in adding a slight deficit of sodium chloride, filtering and titrating the remaining silver with dilute ammonium thiocyanate (J. Amer. Chem. Soc. 1897, 19, 814; *v.* also Chem. Soc. Trans. 1900, 77, 232; Zeitsch. angew. Chem. 1904, 17, 647). (ii.) Titration may be effected with *N*/10-thiocyanate as described under *Preparation of standard solutions.*

Sodium (*v.* Chem. Soc. Trans. 1898, 73, 167).

Sulphur, Acids of. HYDROGEN SULPHIDE. *Iodimetrically.* The gas or a measured volume of solution is absorbed in an excess of *N*/10-iodine, the excess being afterwards titrated with *N*/10-thiosulphate. $H_2S = I_2$. Direct titration with iodine leads to low results (Zeitsch. anal. Chem. 1906, 45, 541).

HYDROSULPHUROUS ACID. *By oxidation.* The sodium salt, used in indigo-dyeing, can be estimated by dissolving it in air-free water in an atmosphere of carbon dioxide, adding a drop of ferrous sulphate, and running in standard potassium ferricyanide solution until a blue colour appears, air being rigidly excluded (Zeitsch. angew. Chem. 1905, 18, 168):

$$Na_2S_2O_4+2K_3Fe(CN)_6=2SO_2+2K_3NaFe(CN)_6.$$

If necessary, a little acetic acid is added to ensure that the liquid shall be acid.

SULPHUROUS ACID. *Iodimetrically.* An aqueous solution of sulphur dioxide is estimated by running it into an excess of standard iodine solution with constant stirring, and not *vice versâ*, since that method causes a separation of sulphur due to the side-reaction:

$$SO_2+4HI=S+2H_2O+2I_2$$

(Annalen, 1887, 242, 94). Sulphites may be accurately determined by adding the powdered salt to excess of *N*/10-iodine, and after the decomposition is complete, titrating back with *N*/10-thiosulphate (J. Soc. Chem. Ind. 1884, 3, 197; 1885, 4, 303)

$$SO_2+I_2+2H_2O = H_2SO_4+2HI.$$

SULPHURIC ACID. (*a*) *Iodimetrically.* The feebly acid boiling dilute sulphate solution is precipitated with an excess of a solution of barium chromate in hydrochloric acid (3–4 grams $BaCrO_4$, 30 c.c. conc. HCl, diluted to 1 litre). Barium sulphate is thus precipitated, and an equivalent of chromic acid liberated. The boiling solution is neutralised with powdered chalk to remove excess of barium chromate, and the chromic acid in the cold filtrate titrated iodimetrically. $CrO_3=SO_3$ (Amer. Chem. J. 1889, 11, 567; Chem. Zeit. 1898, 22, 357).

(*b*) *By precipitation.* (i.) The boiling sulphate solution, slightly acid with hydrochloric acid, is titrated with standard barium chloride until no more precipitate is produced. $Ba=SO_4$ (Chem. News, 1889, 59, 41). A device for readily observing the end-point is described in Chem. Soc. Trans. 1907, 91, 1370. (ii.) Method (i.) may be modified by adding an excess of barium chloride, and determining the excess by adding sodium acetate, acetic acid, and ammonium dichromate, and titrating an aliquot part of the filtrate with *N*/20-ferrous sulphate (Chem. Soc. Trans. 1909, 95, 2198). (iii.) The sulphate is precipitated from dilute solution with excess of benzidine hydrochloride solution as benzidine sulphate, and the precipitate titrated with *N*/10-sodium hydroxide, using methyl orange as indicator (*v.* Zeitsch. angew. Chem. 1907, 20, 9, for details, corrections, &c.).

THIOSULPHURIC ACID. *Iodimetrically.* Thiosulphates are titrated with iodine as in standardising thiosulphate solution (*v. supra*, p. 205); sparingly soluble salts are suspended in water and titrated, shaking vigorously in a stoppered bottle all the time.

PERSULPHURIC ACID. (*a*) *By oxidation.* The solution is acidified with sulphuric acid, a considerable excess of standard ferrous sulphate is added, and then 100 c.c. of hot distilled water (70°–80°). Excess of ferrous salt is then quickly titrated with *N*/10-permanganate. $H_2S_2O_8=2FeO$ (Chem. Soc. Abst. 1900, ii. 45).

(For other methods, *v.* Chem. Zentr. 1900, 435; Amer. J. Sci. 1901, 12, 367; Gazz. chim. ital. 1902, 32, ii. 383; Bull. Soc. chim. 1903, 30, 930.)

Tellurium. TELLUROUS COMPOUNDS. (*a*) *By oxidation.* The solution is rendered alkaline with sodium hydroxide, an excess of *N*/10-permanganate is added, and the excess estimated by acidifying with sulphuric acid, adding *N*/10-oxalic acid in excess, and finishing the titration with permanganate. $2TeO_2=O_2$ (Chem. Soc. Trans. 1891, 59, 238; Amer. J. Sci. 1899, 8, 122).

(*b*) *By precipitation* as tetraiodide in moderately concentrated sulphuric acid solution (Amer. J. Sci. 1896, 2, 271).

(*c*) *Iodimetrically* (*v.* Amer. Chem. J. 1898, 20, 278).

TELLURIC COMPOUNDS. *Iodimetrically.* The tellurate is distilled with concentrated hydrochloric acid in Bunsen's apparatus, the chlorine absorbed in potassium iodide and the iodine set free is titrated with *N*/10-thiosulphate. Telluric anhydride must be previously dissolved in concentrated potassium (not sodium) hydroxide, since it is scarcely attacked by hydrochloric acid. The reduction, which proceeds to tellurous acid, may be also effected by distilling with potassium bromide and dilute sulphuric acid (Zeitsch. anorg. Chem. 1894, 7, 132).

Thallium. *Iodimetrically.* The dilute solution of thallic salt is mixed with excess of potassium iodide, and the iodine liberated is titrated with *N*/10-thiosulphate. $Tl = I_2$ (Compt. rend. 1902, 134, 655).

Tin. STANNOUS SALTS. *Iodimetrically.* The cold hydrochloric acid solution of the stannous salt is titrated with *N*/10-iodine. $Sn = I_2$ (J. Amer. Chem. Soc. 1897, 19, 809). Free exposure of the solution to air must be avoided, since stannous salts readily undergo oxidation; it is preferable to work in an atmosphere of carbon dioxide.

STANNIC SALTS must be reduced before titration with iodine; this may be accomplished by heating the hydrochloric acid solution with iron, or sheet nickel, or with finely powdered antimony (Chem. News, 1901, 84, 167).

Titanium. *By reduction and subsequent oxidation.* It is difficult to obtain accurate results with quantities of titanium dioxide exceeding 0·15 gram. The warm, dilute sulphuric acid solution of titanic salt is reduced to the tervalent condition by means of zinc, aluminium-magnesium alloy, or zinc-aluminium alloy (Zn, 90 p.c. Al 10 p.c., cast in sticks), cooled and rapidly filtered into ferric sulphate solution; the equivalent quantity of ferrous sulphate produced is titrated with $N/10$-permanganate. Ti = Fe (Chem. Zeit. 1907, 31, 399; Amer. J. Sci. 1908, 25, 130; Analyst, 1910, 35, 198; compare J. Amer. Chem. Soc. 1895, 17, 878).

Titanium and Iron (*v. Iron*).

Tungsten. *By reduction and subsequent oxidation.* The solution is reduced by zinc and hydrochloric acid to a condition corresponding to the oxide WO_2, filtered and titrated with a standard ferric solution. The end-point is perceived by the disappearance of the intense blue colour of the intermediate compound corresponding to W_2O_5, the reaction

$$Fe_2O_3+WO_2 = WO_3+2FeO$$

being quantitative (Chem. Soc. Proc. 1909, 25, 227).

Uranium. (*a*) *By reduction and subsequent oxidation.* The solution, containing 20 c.c. of concentrated sulphuric acid in a volume of 125 c.c., is poured upon 100 grams of pure zinc (in sticks 2 cm. long), heated nearly to boiling for 15 minutes, filtered into a large porcelain dish, and the zinc washed with cold dilute sulphuric acid (1 : 10 by volume) till the total volume of solution is 300 c.c. The solution of uranous sulphate, which should be sea-green in colour, is then titrated with $N/10$-permanganate. The solution can also be reduced by passage through a long column of amalgamated zinc; in either case the reduction proceeds a little too far, but oxidation to the uranous state is accomplished during the filtration and washing. High results are obtained by carrying out the experiment in an atmosphere of carbon dioxide.

$$5U(SO_4)_2 = 2KMnO_4 = 10FeSO_4, \text{ or } U = 2Fe$$

(J. Amer. Chem. Soc., 1909, 31, 367; compare *ibid.* 1901, 23, 685; 1906, 28, 1541; Amer. J. Sci. 1903, 16, 229).

(*b*) *Iodimetrically* (*v.* Ber. 1904, 37, 189).

Uranium and Vanadium (*v.* J. Amer. Chem. Soc. 1906, 28, 1443).

Vanadium. (*a*) *By reduction and subsequent oxidation.* (i.) The vanadic solution containing sulphuric acid is boiled with sulphur dioxide until the colour is a pure blue, and the excess of sulphur dioxide then expelled with carbon dioxide; the solution, containing vanadium salt corresponding to the oxide V_2O_4, is then titrated hot with $N/10$-permanganate. (ii.) The sulphuric acid solution is passed through a long column of amalgamated zinc, and the reduced solution collected and titrated as described under *Molybdenum*. In this case reduction proceeds as far as the oxide V_2O_3 (Amer. J. Sci. 1908, 25, 332; compare *ibid.* 1903, 15, 389). (iii.) The solution is evaporated nearly to dryness three times with concentrated hydrochloric acid, when vanadyl chloride $VOCl_2$ is formed; hydrochloric acid is removed by evaporation with sulphuric acid, the solution diluted and titrated with $N/10$-permanganate (Ber. 1903, 36, 3164).

(*b*) *By reduction.* The vanadate solution, hot or cold, and containing hydrochloric or sulphuric acid, is titrated with standard (2 p.c.) stannous chloride (titrated against iodine) until a drop of the solution gives a blue colouration with ammonium molybdate. Reduction proceeds as far as the tetroxide V_2O_4 (Bull. Soc. chim. 1908, 3, 626).

(*c*) *Iodimetrically.* (i.) About 0·3–0·5 gram of vanadate is distilled with 1·5–2·0 grams of potassium bromide and 30 c.c. of concentrated hydrochloric acid, the liberated bromine absorbed in potassium iodide, and the iodine titrated with $N/10$-thiosulphate; $V_2O_5 = Br_2$, the reduction proceeding to the tetroxide (Chem. Zentr. 1890, i. 977; for other iodimetric methods, *v.* Amer. J. Sci. 1896, 2, 185, 355; 1902, 14, 369).

Vanadium and Chromium (*v.* Bull. Soc. chim. 1904, 31, 962).

Vanadium and Uranium (*v.* J. Amer. Chem. Soc. 1906, 28, 1443).

Vanadium and Iron (*v. Iron;* and J. Amer. Chem. Soc. 1908, 30, 1229, 1233).

Zinc. (*a*) *By precipitation.* The chloride solution, containing 3 c.c. of concentrated hydrochloric acid in a volume of 250 c.c., is heated nearly to boiling, and titrated with standard potassium ferrocyanide solution (21·5 grams per litre, titrated against pure zinc) until one or two drops of the solution produce a brown colouration with uranium nitrate (J. Amer. Chem. Soc. 1900, 22, 198; 1904, 26, 4; 1908, 30, 225; Zeitsch. anal. Chem. 1906, 44, 174). The uranium nitrate indicator may be replaced by ammonium molybdate (Chem. Zeit. 1905, 29, 951). It has been recommended to add excess of ferrocyanide, and titrate back with standard zinc chloride (Zeitsch. anal. Chem. 1896, 35, 460).

(For the application of this method to ores and alloys, *v.* J. Amer. Chem. Soc. 1907, 29, 265; Chem. Zeit. 1905, 29, 951; J. Soc. Chem. Ind. 1905, 24, 228, 1278.)

(*b*) *Acidimetrically.* As for *Magnesium, v. supra*, p. 212; and J. Amer. Chem. Soc. 1901, 23, 468.

(*c*) *Iodimetrically.* As for *Magnesium, v. supra*, p. 212; and J. Amer. Chem. Soc. 1900, 22, 353.

Colorimetric Methods.

These methods are especially valuable for the estimation of very small quantities of substances, and are capable of giving very accurate results. The depth of tint produced by some characteristic colour reagent in a given volume of the solution is compared with the tint produced by the same reagent in an equal volume of a solution containing a known quantity of the substance to be determined. The tint in the comparison tube can be varied by varying the proportion of the substance which it contains, and when the tints are equal the quantities of the substance in each tube are also equal. The quantity in one tube is known, and hence that in the other is determined. It is important that the comparison be made under comparable conditions with respect to degree of acidity or alkalinity, proportion of the reagent, and the like. It is also important that the depth of tint should not be materially affected by the presence of other saline substances in the solution under examination.

The following substances may be determined by these methods:—

Lead, with hydrogen sulphide.

Copper, with hydrogen sulphide or potassium ferrocyanide (Carnelley, Chem. News, 32, 308).

Iron, with potassium ferrocyanide (Carnelley, Chem. News, 30, 257).

Iron, with potassium thiocyanate (Thomson, Chem. Soc. Trans. 1885, 493).

Vanadium, with hydrogen peroxide.

Titanium, with hydrogen peroxide (Weller, Ber. 1882, 15, 2593).

Ammonia, by Nessler's solution (*v.* WATER).

Iodine, in solution in carbon disulphide, or with starch.

Nitrates, by phenolsulphonic acid test (*v.* WATER).

Nitrites, by (i.) *m*-phenylenediamine; (ii.) sulphanilic acid and α-naphthylamine (*v.* WATER).

The principle may likewise be applied to the comparison of colouring matters, provided that the solutions are sufficiently diluted (*v.* COLORIMETER).

ULTIMATE ANALYSIS OF CARBON COMPOUNDS.

The majority of carbon compounds contain carbon, hydrogen, and oxygen, or carbon, hydrogen, oxygen, and nitrogen; a smaller number contain one or more of the halogens, or sulphur. There are a still smaller number of organic derivatives of phosphorus, arsenic, antimony, silicon, and other metalloidal and metallic elements, and the metals also occur in the salts of organic acids.

Qualitative Examination.

Carbon is converted into carbon dioxide when the substance is heated with cupric oxide.

Hydrogen. The substance is heated to a temperature below that at which decomposition begins, until all water existing as such is expelled, and is then heated with finely divided and recently ignited cupric oxide; the hydrogen is evolved as water.

Nitrogen. Many carbon compounds containing nitrogen evolve this element in the form of ammonia when heated with caustic soda or soda-lime, but this test is not applicable to nitro-, nitroso-, azo-, and diazo- derivatives.

Many nitro-, nitroso-, and diazo- derivatives evolve oxides of nitrogen, with or without explosion, when heated.

Nitrogen in all classes of carbon compounds, with the exception of the diazo- compounds, may be detected by heating the substance with metallic sodium or potassium, together with some sodium carbonate if the substance is explosive. The nitrogen is converted into alkali cyanide, and the cooled mass is extracted with water and the cyanogen detected by the Prussian-blue test, which consists in adding ferrous sulphate to the alkaline solution after filtration, warming gently and then acidifying. Nitrogenous carbon compounds containing sulphur yield, when heated with sodium, a thiocyanate, and the Prussian-blue test cannot be used. A large excess of potassium is recommended in this case, when it is stated that sulphur does not interfere (Täuber, Ber. 1899, 32, 3150). A mixture of potassium carbonate (138 parts) and magnesium powder (72 parts) has been recommended for general use in detecting nitrogen even in the case of diazo- derivatives and stable pyrrole compounds (*v.* Ber. 1902, 35, 2523; Gazz. chim. ital. 1904, 34, [2] 359). This mixture is, however, found to take up nitrogen from the atmosphere (Ellis, Chem. News, 1910, 102, 187).

Halogens are detected by heating the substance with pure lime or pure soda-lime, extracting with water, slightly acidifying with nitric acid, and testing with silver nitrate. Highly nitrogenous compounds, when heated with lime, are apt to yield calcium cyanide; hence the supposed precipitate of silver halide should always be tested for cyanide (*v. Separation of cyanide and chloride*), unless nitrogen is known to be absent. With soda-lime no cyanide is formed. The substance may also be heated with sodium or potassium as in testing for nitrogen; iodine and bromine are detected by acidifying, adding chlorine water, and shaking up with chloroform, which becomes purple or brown. The supposed silver chloride should, however, always be tested for cyanide.

Sulphur and phosphorus in non-volatile substances are detected by fusing with caustic soda or potash mixed with about one-fifth its weight of potassium nitrate, or by heating with sodium peroxide diluted with sodium carbonate; in either case the product is tested for sulphuric or phosphoric acid. Volatile or non-volatile substances may be oxidised by heating in a sealed tube at 150°–300°, according to circumstances, with fuming nitric acid of sp.gr. 1·5. Sulphur and phosphorus are oxidised to sulphuric and phosphoric acid respectively.

Sulphur is also detected by heating the substance with sodium, extracting with water, and adding sodium nitroprusside, when a brilliant violet colouration indicates the presence of alkaline sulphide.

Arsenic and antimony are detected by fusing the substance with equal weights of sodium carbonate and sodium peroxide, extracting with water, acidifying, and passing in hydrogen sulphide. Other appropriate tests for these two elements may be applied.

Quantitative Determinations.

Carbon and hydrogen in absence of nitrogen, halogens, &c.

The simplest and most convenient method for general purposes is to burn the compound in a glass tube in a current of oxygen, assisted by cupric oxide; the carbon is converted into carbon dioxide, which is absorbed by caustic potash; the hydrogen is converted into water, which is absorbed by calcium chloride or concentrated sulphuric acid.

Erlenmeyer's modification of Von Babo's furnace is frequently employed. The heat is supplied by a row of 20–25 Bunsen burners, each of which is provided with a tap and a perforated collar for regulating the supply of air. The flames strike the under side of a semicircular fireclay or sheet-iron trough or gutter in which the combustion tube rests on a layer of magnesia or asbestos. Inclined at an angle over this gutter on either side is a row of fireclay tiles by which the flame is reverberated upon the upper part of the glass tube, which is thus heated all round. Each tile can be pulled back and rested against an iron rail which runs down each side of the furnace, and thus any part of the tube can be readily examined, and moreover the tiles can be made to assist in regulating the temperature.

In Hofmann's furnace the tube is heated by two double rows of perforated cylindrical fireclay burners placed over ordinary fish-tail burners. The tube rests upon the top of a central row of much shorter burners. The burners are inclosed by flat vertical tiles, and flat tiles are laid horizontally on the top.

In the Glaser furnace the heat is provided by a row of Bunsen burners. The tube is supported by a series of semicircular perforated iron plates, placed close together. The flames strike the bottom of these plates, and then pass through the perforations and strike against the fireclay covers, by which they are reverberated on the tube, so that the latter is heated from the top and sides as well as from the bottom. The tube is usually wrapped round with wire gauze. This furnace will give higher temperatures than the Erlenmeyer furnace, but consumes more gas.

A more modern type of combustion furnace which gives very high temperatures with a small consumption of gas has been introduced by Fletcher. The furnace itself consists of six separate hollow fireclay blocks 6 inches in length and of the same height, which are placed end to end, so as to give a total length of 3 feet. The combustion tube is supported on a fireclay trough placed along the top of the row of furnace blocks which are each pierced along one side with five holes leading to a hollow space immediately below the trough. The main gas-supply pipe is a brass tube of square section which is raised about 1½ inch above the stone bench by terminal brass supports; it carries thirty burners projecting at right angles from it in a slanting direction, so that their nozzles reach upwards to the perforations in the furnace blocks, the centres of these holes being about 3½ inches above the bench. Each furnace block is therefore heated by five burners, and reverberation is ensured by small semicircular fireclay arches, three of which fit loosely on each of the furnace blocks. Owing to their oblique position, the burners are readily kept clean, the brass heating arrangement is quite separate from the earthenware furnace, and the taps and lower parts of the burners are protected from the heat of the furnace by a brass shield running along the whole length of the main gas pipe. The furnace can be built up in shorter lengths by using fewer of the furnace blocks, of which two are represented in Fig. 16.

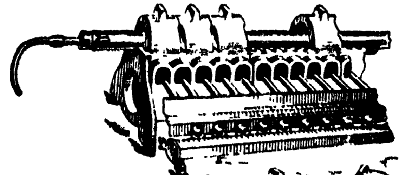


FIG. 16.

To avoid the necessity for using an indiarubber stopper between the combustion tube and the water-absorption apparatus, Marek suggests a mercury joint made by drawing out the combustion tube to a conical end, and fixing round this a knee tube by means of asbestos and fused silver chloride. The knee joint, which is loosely filled with silver ribbon, fits into a bell-shaped tube dipping under mercury (J. pr. Chem. 1907, [2] 76, 180).

The combustion tube should consist of infusible potash or Bohemian glass 1·5–2 mm. thick, with an internal diameter of 12–15 mm. It should be of such a length that it projects about 2 cm. from each end of the gutter or trough. Pieces of copper wire gauze about 2 cm. broad, heated in a flame to remove grease, are rolled up into plugs which fit moderately tightly in the tube, and one of these plugs is pushed into the tube to a distance of about 25 cm. from one end. The tube is then filled with freshly ignited granular cupric oxide to within 5 or 6 cm. of the other end, and a second plug is inserted. The granules of cupric oxide should be fairly regular in size, and 1·5–2 mm. cube. Another plug about 10 cm. long is made by rolling a piece of copper gauze round a stout copper wire 12 cm. long, and bending the projecting end of the latter into a loop by means of which it can be withdrawn from the tube. This plug is placed in the other end of the tube behind the boat. The end of the tube nearest to the copper oxide is fitted with a dry caoutchouc stopper perforated to receive the tube of the absorption apparatus; the other end is closed by a similar stopper, which carries a piece of tubing of very narrow bore, which is connected with the apparatus for drying the oxygen.

The substance to be analysed is contained in a platinum or porcelain boat about 70 mm. long and 8 mm. deep, of such diameter that it slides easily in the combustion tube. It may conveniently be inclosed in a small well-corked tube while being weighed.

The water is absorbed by granulated anhydrous calcium chloride, which is treated with a current of dry carbon dioxide, and then with a current of dry air to convert any calcium oxide present into carbonate, and thus prevent the absorption of carbonic dioxide.

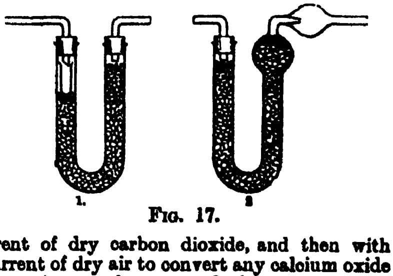


FIG. 17.

The calcium chloride is contained in a U-tube provided with a small side bulb for condensing the water, the tube from this bulb fitting directly into the cork in the combustion tube, whilst the other limb of the U-tube is closed by a caoutchouc cork carrying a narrow tube bent at a right angle and connected with the potash bulbs (Figs. 18

and 19). In the absence of the side bulb, each limb of the tube is closed by a caoutchouc cork carrying a narrow tube bent at a right angle, one of these tubes fitting directly into the cork of the combustion tube, and the other being connected with the potash bulbs. A small test-tube, 2–3 cm. long, placed in the upper part of the first limb of the U-tube, collects the greater part of the water, and thus protects the calcium chloride (No. 1, Fig. 17). (For other forms of calcium chloride tubes, v. Chem. Soc. Proc. 1906, 22, 87; Chem. Zeit. 1907, 31, 342.)

A U-tube containing pumice moistened with strong sulphuric acid may also be used to collect the water, but bulbs filled with the acid must not be used, since it dissolves an appreciable quantity of carbon dioxide.

The carbon dioxide is absorbed in a strong solution of potassium hydroxide made by dissolving this substance in an equal quantity of water. The solution is contained in 'potash bulbs,' of which there are many forms. Geissler's form is the most convenient, since it will stand on its own base (No. 2, Fig. 18). Liebig's original form (No. 1) is still used, but the more recent form devised by Bender (Fig. 19) secures efficient absorption, and is convenient for weighing, as it stands either on its own base or on an aluminium foot.

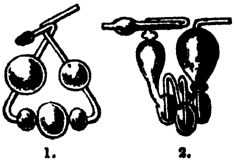

1. 2.

Fig. 18.

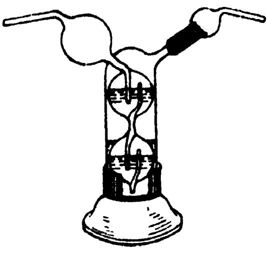


Fig. 19.

The Geissler or Liebig bulbs must contain such a quantity of caustic potash solution that it washes up to a certain extent in the last bulb, but yet is not sufficient to fill the large first bulb in case a vacuum is produced by rapid absorption of the gas. In addition to the potash bulbs, a U-tube filled with granulated soda-lime, with a layer of calcium chloride 2 cm. deep in the upper part of each limb, is used to absorb the last traces of the gas and any small quantity of moisture that may be given off from the caustic potash solution. Two such soda-lime tubes may be used in place of potash bulbs. (For other forms of carbon dioxide absorption tubes, v. Chem. Zeit. 1905, 29, 569; 1907, 31, 342; 1908, 32, 77; Amer. Chem. J. 1906, 35, 309; Ann. Chim. anal. 1907, 12, 318; Chem. Soc. Proc. 1908, 24, 182.)

The tube containing the soda-lime is connected with a U-tube filled with calcium chloride, to protect the absorption apparatus from moisture; this is especially needful when the air is drawn through the apparatus by means of an aspirator.

The oxygen or air used in the combustion is freed from carbon dioxide by passing through a strong solution of caustic potash. If compressed oxygen is employed, it is advisable to pass it first through a short length of heated combustion tube containing cupric oxide, in order to burn out any carbonaceous impurity. The air or oxygen is then dried by passing through dry calcium chloride or through pumice moistened with concentrated sulphuric acid, the same desiccating agent must be used to dry the gas as is employed to collect the water produced during the combustion.

The oxygen is dried by passing it through two long U-tubes containing calcium chloride. Instead of the U-tubes we may use a tall cylinder with the lower half filled with soda-lime and the upper with calcium chloride.

The oxygen required for combustions in the open tube may be prepared from potassium chlorate and manganese dioxide and stored over water in gasholders of moderate capacity. The gas may also be generated as required by the following method, which furnishes the gas under sufficient pressure for use in combustions. A solution of 25 grams of potassium permanganate in 500 c.c. of water, and 50 c.c. of sulphuric acid is introduced drop by drop into a litre flask containing 500 c.c. of hydrogen peroxide (10 vols.). The gas contains chlorine and ozone, which are removed during its passage through the purifiers (Bull. Soc. Chim. 1907, [4] 1, 501).

The operation.—The tube is placed in the furnace and connected at one end with the drying apparatus and at the other with the calcium chloride guard tube, but not with the absorption apparatus. It is gradually heated to redness, a current of dry oxygen is passed through for half an hour to remove all moisture and organic matter, and the tube is allowed to cool. When a combustion tube is being used for the first time or after a long interval, it is advisable to carry out a blank experiment by putting on the absorption apparatus and heating the tube for some time in a stream of dry oxygen. If the tube is ready for the analysis, the weight of the absorption tube and apparatus should be constant. The solid or non-volatile liquid substance is now weighed into the platinum boat, which is introduced into the tube by removing the long copper plug at the back, and the latter is then replaced. The front end of the tube is then connected with the absorption apparatus, and the other end is connected with the drying tubes and the oxygen reservoir. The burners under the front part of the tube are now lighted and the temperature gradually raised until the tube is at a dull-red heat to within 12 cm. of the boat. The tube in contact with the stopper at the front end should be so hot that it can only just be touched by the finger, and this temperature should be maintained throughout the operation by regulating the first two burners, in order to prevent condensation of moisture without decomposing the stopper. If any water should condense, it may be volatilised by bringing one of the hot tiles close over the tube. The last two or three burners under the long copper plug at the back are now lighted and the temperature gradually raised to dull redness, whilst at the same time the copper oxide is heated to within 5–6 cm. of the boat, and a current of oxygen is passed through the tube at the rate of a bubble every two seconds. One of the burners under the boat is then lighted and the boat very gradually heated, combustion being regulated so that the bubbles passing into the potash bulbs can easily be counted. When the substance is completely carbonised, the temperature of the boat is raised and the current of oxygen increased to a bubble per second. Towards the close of the operation the boat is heated to redness and a somewhat more rapid current of gas is passed. It is not necessary to heat the tube above redness, and a higher temperature produces distortion. When combustion is complete, the current of oxygen is continued for a short time to drive out all carbon dioxide and reoxidise any reduced copper. When the oxygen bubbles through the potash bulbs at the same rate as through the drying apparatus, the oxygen reservoir is disconnected and a current of air is drawn through the whole apparatus to expel the oxygen. At the same time the tube is gradually cooled and is ready for a second operation. If the tube is carefully heated and cooled, it may be used for a very large number of analyses. The absorption apparatus is disconnected and weighed. All the weighings should be made without the plugs of caoutchouc tubing and glass rod which are used to protect the contents of the tubes and bulbs from the air. When several analyses are being made of substances which burn only with difficulty, the entire heating may with advantage be carried out in a current of oxygen, and some saving of time is effected by weighing the absorption apparatus filled with oxygen.

Volatile liquids are inclosed in a small thin cylindrical glass bulb 3 cm. long, with a capillary neck, readily made by drawing out a piece of wider tubing. The bulb is weighed, heated, and the capillary tube immersed beneath the liquid. As the tube cools a small quantity of the liquid enters. This is heated to boiling, and when the air is expelled the end of the tube is again placed in the liquid, and when the vapour condenses the bulb is completely filled. If the liquid is very volatile, the capillary end may be sealed before weighing the tube, but usually this is not necessary. The bulb is placed in the boat with the capillary end open and directed towards the copper oxide. Combustion is conducted as already described, but much greater care is required, especially if the liquid is very volatile. The front part of the copper oxide must be quite red-hot before the liquid begins to volatilise, and it is advisable that the bulb be empty before the copper oxide near the boat is heated. With an iron gutter sufficient heat is conducted to vapourise volatile liquids, but in other cases a very low flame may be used, or one of the hot tiles may be held over the boat. In all cases it is difficult to prevent diffusion of vapour into the back of the tube and even into the drying apparatus. The long copper plug at the back increases the speed of the current by decreasing the diameter of the passage, and the narrow diameter of the entrance tube assists in a similar manner, but in all cases of the analysis of a volatile substance a slow current of air should be passed almost from the beginning. Later, oxygen should be passed, but not too soon, otherwise an explosive mixture may be formed. The open tube, in fact, does not yield such satisfactory results with volatile liquids as with other substances, and in such cases combustion should be made by the following method.

Liebig's original method as modified by Bunsen. Granular cupric oxide and some of the finely divided oxide are heated strongly, and while still hot are placed in flasks with long necks which are then tightly corked. The combustion tube is drawn out at one end in the manner shown in the figure, and sealed at the point *a*.

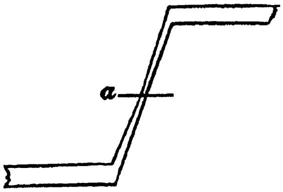


FIG. 20.

A layer of granular cupric oxide about 10 cm. long is first introduced by placing the combustion tube in the neck of the flask (Fig. 21) containing it, and then 2–3 cm. of the finely divided oxide. The substance (about 0·5 gram) is now introduced from a long narrow weighing tube which can be inserted into the mouth of the combustion tube, and 5–6 cm. of the finely divided oxide is added and intimately mixed with the substance by means of a long copper wire, the lower end of which has two twists like a corkscrew (Fig. 22). The wire and sides of the tube are rinsed with some of the oxide, and the tube is filled with the granular oxide to within 5–6 cm. of the top, and a plug of cupric gauze inserted. Every care must be taken to prevent absorption of moisture by the cupric oxide. The remainder of the operation is conducted as described above, and when combustion is complete the drawn-out end of the tube is connected with a drying apparatus, the tip broken off inside the caoutchouc tube, and a current of oxygen and afterwards of air passed through the apparatus.

FIG. 21.

FIG. 22.

In whichever way the combustion is made it is found that the percentage of hydrogen is always about 0·1–0·15 too high, a result attributed to the difficulty of perfectly drying the cupric oxide, &c. It is frequently stated that an open tube rarely gives correct results the first time it is used; but this is solely due to neglect of the precaution of first heating in a current of oxygen.

Combustion with lead chromate. Substances such as graphite, resins, &c. which are oxidised with great difficulty, should be burnt with lead chromate, or in extreme cases with lead chromate containing 10 p.c. of potassium bichromate; these oxidising agents can be employed in either open or closed combustion tubes. The chromate is precipitated by adding potassium bichromate to a solution of lead nitrate, washed, dried, fused, and then granulated. It is heated immediately before being used, and the tube is filled in the same manner as with copper oxide in B. The efficiency of the lead chromate depends mainly on the fact that at a high temperature it fuses. After being used it is heated with nitric acid in order to remove the reduced oxides, and is washed, dried, and again ignited.

Carbon and hydrogen in presence of nitrogen, halogens, &c. When nitrogen is present it is partly converted into nitrogen oxides, which are absorbed by the caustic potash. In order to avoid this source of error, the front of the tube contains plugs of copper wire gauze or a layer of granulated metallic copper 12–15 cm. in length reduced in carbonic oxide. The copper is heated to redness throughout the operation, and the nitrogen oxides are decomposed with absorption of oxygen and liberation of nitrogen. A silver gauze plug is preferable to the copper, because if the latter is reduced in hydrogen, it is apt to retain water, and if in methyl alcohol, it may also contain carbon (Zeitsch. anal. Chem. 1906, 14, 741).

Perkin (Chem. Soc. Proc. 1880, 37, 457) employs precipitated manganic oxide made into a paste with a saturated solution of potassium chromate containing 10 p.c. of dichromate, dried and granulated. A layer of this mixture 15 cm. long is placed in the front of the tube and heated to 200°–250° C. All nitrogen oxides are absorbed, but if the mixture is heated too strongly they are partially expelled. After each analysis the manganic oxide is heated more strongly whilst a current of air is passed through the tube, and the nitrogen oxides are more or less completely driven off.

The halogens, when present, form halide copper salts, which are somewhat volatile and are liable to be carried into the absorption apparatus. In such cases the front layer of copper may be replaced by silver foil or gauze, which decomposes the nitrogen oxides and also absorbs the halogens. Compounds of this kind may also be burnt by means of lead chromate, (*v. supra*), or a mixture of the substance with lead chromate may be placed in a porcelain boat and burnt in a current of oxygen in the usual way (*cf.* Amer. Chem. J. 1906, 35, 531).

Sulphur forms sulphur dioxide, which is absorbed by caustic potash. Compounds containing this element may be burnt with lead chromate, care being taken that the front of the tube is not too hot; or the front of the tube may contain a somewhat longer layer of manganic oxide and potassium chromate, the front half being kept at 200°–250° to absorb nitrogen oxides, whilst the rear half is heated to dull redness and absorbs the sulphur dioxide (Perkin, *l.c.*).

Combustion in presence of a contact substance. The use of a special combustion furnace may be obviated by bringing a mixture of oxygen and the vapour of the organic substance heated to a suitable temperature, into contact with some active material, such as platinum, platinised quartz, platinised asbestos, palladium, or even finely divided copper oxide. This process, which has been applied successfully by Dennstedt and his collaborators to a varied series of organic substances, is carried out in a hard-glass or quartz combustion tube, about 86 cm. in length and 16–18 mm. in diameter, the contact material being placed about the middle of the tube. Platinised quartz is prepared by soaking thoroughly clean and dry quartz fragments in an alcoholic solution of pyridine platinichloride and igniting them over the blow-pipe. A layer of about 3 cm. of this material can be used in the combustion, or platinum foil or wire may be employed, one of the most efficient forms of this metal being a six-rayed star of platinum foil, about 10 cm. in length. The combustion is most conveniently effected in a double supply of oxygen. The boat containing the substance is placed in the hard-glass inner tube (18 cm. in length) shown in Fig. 23, which is open at one end and at the other terminated by a wide capillary tube, through which a current of dry oxygen can be introduced. This inner tube has a diameter of about 14 mm., and oxygen can be passed through the annular space by means of the T-tube fitting over the capillary tube as shown in the figure.

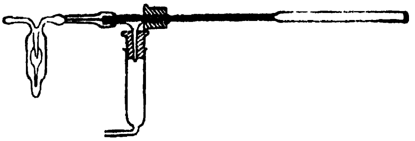


FIG. 23.

By means of this apparatus the supply of oxygen required for vaporising and burning the substance can be carefully regulated. When the organic compound contains nitrogen, sulphur, or halogens, a large boat containing lead peroxide is placed in the combustion tube and heated to 300°–320°. The sulphur is absorbed in the form of lead sulphate, and may be estimated by extracting the lead peroxide with 5 p.c. sodium carbonate solution, and estimating the sulphate in the filtrate. The estimation of chlorine and bromine may be similarly effected. Iodine is not entirely absorbed by lead peroxide, and, accordingly, 'molecular' silver must be employed to take up this element (Dennstedt, Zeitsch. angew. Chem. 1905, 18, 1134; 19, 517; Chem. Zeit. 1905, 29, 52; 1909, 33, 769; Analyst, 1905, 135; Ber. 1908, 41, 600; Baumert, Ber. 1907, 40, 3475). Walker and Blackadder recommend a furnace 60 cm. long, with granular copper oxide partly placed in the combustion tube and partly mixed with the weighed substance. The combustion is carried out in about 30 minutes, and the tube can be heated with Bunsen burners on an ordinary working bench (Chem. News, 1909, 99, 4; *cf.* Marek J. pr. Chem. 1906, 73, 359).

Electrical method. In this process the electric current is used as the source of heat, and platinum as the catalyst. A Dennstedt inner tube is employed to contain the boat Z with the weighed substance, and the spiral of platinum-iridium wire NJ is wound round a porcelain or quartz tube held in position in the combustion tube by a nickel tube DE, passing through the indiarubber stopper C. The coil is heated to redness by the passage of the current through DKJOP, and the absorption apparatus is fitted on to the outer end of the nickel tube DE. A divided stream of oxygen is employed as in the Dennstedt process, and the time required for complete combustion varies from 15 to 40 minutes.

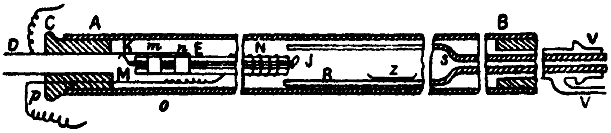


FIG. 24.

The consumption of electrical energy in this method of carrying out combustions is small, amounting to about 3·6 amperes at 54 volts (194·4 watts) during the time when the highest temperature is obtained (Breteau and Lerona, Bull. Soc. chim. 1908, [4] 3, 15; *cf.* B. Blount, Analyst, 1905, 30, 29; Morse and Taylor, Amer. Chem. J. 1905, 33, 591; Morse and Gray, Amer. Chem. J. 1906, 35, 451; Carrasco and Plancher, Gazz. chim. ital. 1906, 36, 492; Lippmann, Chem. Zeit. 1905, 29, 487, 174; Tucker, J. Amer. Chem. Soc. 1907, 29, 1442).

Nitrogen. This element is determined in the form of ammonia (Will and Varrentrapp, Ruffle, Kjeldahl), or in the form of nitrogen gas, which is collected and measured, the weight being calculated from the volume (Dumas, Maxwell Simpson).

A. *Will and Varrentrapp's method.* The substance is heated with soda-lime and the nitrogen is evolved as ammonia, which is absorbed in hydrochloric acid and precipitated as ammonium platinichloride or estimated volumetrically. This method is not applicable to azo-, diazo-, nitro-, and nitroso- derivatives, and to certain albuminoid substances.

Soda-lime is prepared by slaking 2 parts of good quicklime with a strong solution of 1 part of sodium hydroxide free from nitrates or sulphates. The mixture is dried by heating in an iron vessel, granulated, and preserved in well-closed bottles. A mixture of equal parts of calcium hydroxide and anhydrous sodium carbonate may also be used.

A glass tube about 50 cm. long and 12 mm. diameter, sealed at one end, is filled to a depth of about 5 cm. with a mixture of anhydrous oxalic acid and granular soda-lime, and a short plug of recently ignited asbestos is inserted. The substance is intimately mixed with sufficient finely powdered soda-lime to form a layer about 15 cm. long, and is quickly introduced into the tube. The mortar is rinsed with a small quantity of soda-lime, which is also put in the tube, and the latter is then filled with granular soda-lime to within 5 cm. from the end and a loose asbestos plug inserted. The tube is tapped to form a channel over the powdered soda-lime for the escape of the gases, and is placed in a furnace, which may be considerably shorter than that used in the estimation of hydrogen and oxygen. The combustion tube is attached by means of a perforated cork to an apparatus for absorbing the ammonia. This may consist of the bulbs originally devised by Will and Varrentrapp, or of an ordinary bulb U-tube. Winkler has devised a combination of bulb and flask which is especially convenient for estimations by titration, since the liquid need not be transferred. Ordinary dilute hydrochloric acid or a definite volume of standard acid is placed in the bulb. The tube is gradually heated to redness, beginning at the end near the U-tube, and when decomposition is complete the oxalic acid at the back is heated, and the ammonia in the tube is driven out by the current of carbonic oxide and carbon dioxide. The excess of acid is then determined by standard alkali; or the liquid is evaporated with platinic chloride as in an ordinary estimation of ammonia, and the precipitate is washed with ether containing a small quantity of alcohol, dried, heated in a crucible till completely decomposed, and the nitrogen calculated from the weight of the residual platinum. $Pt = N_2$. The nitrogen frequently forms volatile bases other than ammonia, and hence the platinum precipitate cannot be weighed as such. The ratio of platinum to nitrogen is, however, the same in all cases. The precipitate is washed with ether, because if such bases are present, it may be soluble in alcohol.

It is important that the front part of the tube be heated sufficiently to secure complete decomposition, but the temperature must not be too high, otherwise part of the ammonia itself is decomposed, and the results are too low. Substances rich in nitrogen should be mixed with some pure sugar in order to dilute the ammonia and prevent too rapid absorption.

Various modifications of Will and Varrentrapp's method have been introduced in order to make it more generally applicable, but these processes have been superseded by Kjeldahl's method (*cf.* Ruffle, Chem. Soc. Trans. 1881, 39 87; Arnold, Ber. 1885, 18, 806).

B. *Dumas' method.* In this process the hydrogen and carbon are burnt by means of cupric oxide and the liberated nitrogen collected and measured. A glass tube 80 cm. long, 12 to 15 mm. diameter, sealed like a test-tube at one end, is filled to a length of 12–15 cm. with dry sodium hydrogen carbonate, 4 cm. of cupric oxide is added, and then an intimate mixture of the substance (0·3–0·6 gram) with cupric oxide, then the cupric oxide used to clean the mortar, a layer of granular cupric oxide, and finally a layer of reduced granulated copper or copper-wire gauze not less than 15 cm. in length. The tube is connected by means of a cork and bent tube with an apparatus for collecting the nitrogen. The sodium hydrogen carbonate is first heated until all air is expelled and the issuing gas is completely absorbed by potash solution. The copper is then heated to redness, the heat being gradually applied to the whole tube as far as the carbonate. When combustion has ceased, the carbonate is again heated until all the nitrogen has been expelled.

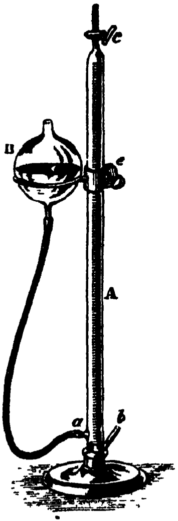


FIG. 25.

The most convenient form of apparatus for collecting the nitrogen is that devised by H. Schiff (Zeitsch. anal. Chem. 7, 430), or a similar form described by Groves (Chem. Soc. Trans. 1880, 37, 500). The former consists of a burette, A, fitted with a heavy foot and provided with a stop-cock, *c*, at the top. Close to the bottom is a tubulus, *b*, inclined at an angle of about 45°, and on the other side is another tubulus, *a*, connected by means of a caoutchouc tube previously soaked in paraffin with a globular reservoir, B, which is attached to the burette by a clip, and the height of which is readily adjusted. Mercury is poured into the burette through the lower tubulus to a height of 2 or 3 mm. above the lower opening, and the reservoir is then filled with a solution of caustic potash in its own weight of water, the lower tubulus being closed with a cork. The stopcock is opened and the reservoir raised until the burette is completely filled with the alkaline solution. The stopcock is then closed and the reservoir lowered to the bottom of the burette. The tubulus may now be opened without the mercury or alkaline solution being forced out. When the air has been expelled from the combustion tube the end of the delivery tube is inserted through the tubulus and the nitrogen collected. At the close of the operation the temperature of the gas is allowed to become constant, the reservoir is raised so that the level of the liquid is the same as in the burette, and the volume of the nitrogen is read off, together with the temperature and the height of the barometer. The weight of the nitrogen, P, is then calculated from the volume by means of the formula

$$P = \frac{V(B-f)0{\cdot}001251}{(1+0{\cdot}00366t)760},$$

where V is the observed volume, B the height of the barometer, f the tension of aqueous vapour at the temperature t, and 0·001251 the weight of 1 c.c. of nitrogen at 0° and 760 mm.

Gatterman (Zeitsch. anal. Chem. 24, 57) collects the nitrogen in an apparatus similar to Schiff's, but not graduated. A bent tube of small diameter completely filled with water is attached to the jet of the burette by means of caoutchouc tubing. By closing the lower tubulus, raising the potash reservoir, and opening the stopcock, the gas is driven over into a graduated tube standing over water, and is measured. The error due to the unknown vapour tension of the potash solution is thus avoided, but the vapour tension of the water at the particular temperature must of course be taken into account. Other forms of apparatus are described by Zulkowsky (Annalen, 1876, 182, 296; Roscoe and Schorlemmer's Chemistry, 3, pt. 1, 74) and Schwarz (Ber. 1880, 13, 771).

C. *Maxwell Simpson's modification of Dumas' method* (Chem. Soc. Trans. 1853, 6, 290; Annalen, 1855, 95, 74). In order to avoid the formation of carbonic oxide and nitric oxide, the substance is burnt with a mixture of cupric oxide and mercuric oxide. Into a tube similar to that used in Dumas' method is introduced about 12 grams of manganese carbonate or granulated magnesite mixed with 2 grams of precipitated mercuric oxide, followed by a plug of asbestos. Another gram of mercuric oxide is introduced, and then an intimate mixture of 0·5 gram of the substance with 45 parts of a previously prepared and thoroughly dry mixture of 4 parts of ignited cupric oxide and 5 parts of precipitated mercuric oxide. The mortar and the sides of the tube are rinsed with a similar mixture and another asbestos plug is introduced. A layer of granular cupric oxide about 9 cm. in length and a layer of not less than 20 cm. granulated copper, kept in position by another asbestos plug, fill the remainder of the tube. After the air has been expelled by heating the manganese carbonate or magnesite, the tube is gradually heated to redness, beginning from the front. The metallic copper not only decomposes nitrogen oxides, but also absorbs the excess of oxygen. The gas is collected as in Dumas' method, the magnesite or manganese carbonate providing the carbon dioxide.

Certain organic compounds (*e.g.* hydroaromatic series), when analysed for nitrogen, evolve a portion of their carbon as methane, which, being burnt only imperfectly, adds to the volume of the nitrogen. In these cases lead chromate is recommended as the oxidising agent, or the substance may be mixed with cuprous chloride and copper oxide (Haas, Chem. Soc. Proc. 1906, 22, 81).

Various modifications of Dumas' process have been proposed. Thudichum and Wanklyn use a mixture 5 parts of normal sodium carbonate and 13 parts of fused potassium bichromate in place of sodium hydrogen carbonate. Groves (*l.c.*), with a view to using the same tube repeatedly, places the mixture of carbonate and bichromate in a small tube connected with the combustion tube by an indiarubber joint. The portion of the cupric oxide mixed with the substance is separated from the layer remaining always in the tube by means of a tight plug of asbestos and copper gauze, the latter keeping a free passage for the gas.

The combustion tube may be open at both ends, the rear being connected with an apparatus for generating carbon dioxide, but special precautions must be taken to obtain this gas free from air (*v.* Warington, Chem. Soc. Trans. 1882, 41, 346).

The carbon dioxide required for this modification of Dumas' process may be generated in a Kipp's apparatus by the action of hydrochloric acid on marble or calcite. These minerals should, however, be boiled with water before being used, in order to free them from air. The dioxide may also be generated by dropping a concentrated solution of potassium carbonate (sp.gr. 1·5) into a mixture of water and concentrated sulphuric acid. A convenient apparatus in which to effect this operation is shown in the accompanying figure (Young and Caudwell, J. Soc. Chem. Ind. 1907, 26, 184). The carbonate solution flows from the dropping funnel into the mercury trap and out into the Woulff's bottle through the small hole *a*. The rate of evolution is regulated by the exit tap, and *s* is a safety tube.

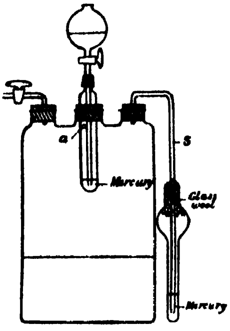


Fig. 26.

In both Dumas' method and Simpson's modification the combustion tube may be drawn out at the front end and connected with a Sprengel mercury pump by glass tubing joined by short pieces of caoutchouc tubing, the joints being surrounded by short wide tubes filled with water or glycerol. A bulb is blown on the horizontal part of the glass tube at the end near the combustion tube, and this bulb is kept cool during the operation, and serves to condense the water which is formed. The combustion tube is made vacuous, and when no more air issues from the end of the pump, the combustion is conducted in the ordinary way, the gas which is evolved being pumped out by the Sprengel pump and collected in a suitable tube. No magnesite need be used. The copper oxide keeps the exhausted tube from collapsing when heated.

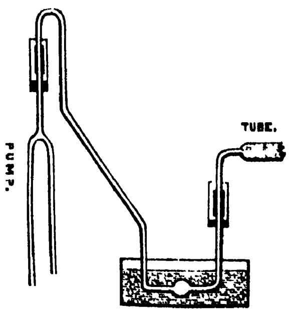


Fig. 27.

In many cases, especially with nitro- derivatives, the gas generated in the exhausted tube is a mixture of nitrogen with nitric oxide, the latter being sometimes present in considerable quantity. It is advisable, therefore, to decompose the nitric oxide by using either a layer of reduced copper or a long plug of silver gauze placed between the copper oxide and the exit, and by keeping this material heated throughout the combustion.

Liquids in which nitrogen is to be determined may be enclosed in bulbs which are dropped into the combustion tubes as in the determination of hydrogen and oxygen.

The copper oxide used in nitrogen determinations should be prepared by heating metallic copper in air and never by ignition of the nitrate, since in the latter case it is apt to contain basic nitrates which evolve nitrogen on heating.

The copper used in nitrogen determinations, &c., should not be reduced in hydrogen, since it is liable to occlude this gas. It may be reduced in the mixture of carbon monoxide and carbon dioxide obtained by heating oxalic acid with strong sulphuric acid. Plugs of copper gauze may also be reduced by heating them to redness and dropping them into a test-tube containing a few drops of formic acid or methyl alcohol. The reduced copper is carefully dried at 100°–110°.

When no carbonate is used and the gas is simply pumped out of the tube and collected over mercury, it consists of a mixture of carbon dioxide and nitrogen. If the former is estimated by absorption with caustic potash, a determination of the carbon may be combined with that of nitrogen.

Jannasch and Meyer have described a method for the simultaneous estimation of carbon, hydrogen, and nitrogen (Ber 1886, 19, 949; Annalen, 1886, 233, 375; Zeitsch anal. Chem. 1887, 26, 86; *cf.* Bull Soc. chim. 1905, 33, 951).

D. *Kjeldahl's method* (Zeitsch. anal. Chem. 1883, 22, 366) The substance is heated with concentrated sulphuric acid to a temperature approaching the boiling-point of the latter, and when decomposition is complete, an excess of solid potassium permanganate is added. The nitrogen is thus converted into ammonium sulphate, which is then distilled with excess of alkali and the ammonia collected and estimated. This method is economical, requires no combustion furnace or special apparatus, is rapid, and requires comparatively little attention, so that a large number of determinations can be carried on at the same time. The substance need not be in a very fine state of division, and the method is especially suitable for liquid and pasty substances such as extracts.

It is important that the sulphuric acid employed for these determinations should be protected from ammonia, and the caustic soda solution should be well boiled in order to expel any ammonia which it may contain. The purity of the reagents is best ascertained by making an experiment with pure sugar. If a small quantity of ammonia is present, the same quantity of the reagents should be used in each experiment, and a correction made for the ammonia which they contain.

In order to prevent bumping during distillation a small piece of zinc may be placed in the flask, but it is essential that the soda should be free from nitrates and nitrites, which would be reduced and yield ammonia.

The time required for the operation may be considerably shortened by using sulphuric acid containing sulphuric anhydride or phosphoric anhydride.

The method as thus carried out is applicable to all substances which can be analysed by Will and Varrentrapp's process, and to many others.

Heffter, Hollrung, and Morgen (Zeitsch. f. Chem. 8, 432) treat 1·0–1·5 grams of substance with 20 c.c. of a mixture of 4 vols. ordinary sulphuric acid and 1 vol. of fuming acid, and 2 grams of phosphorus pentoxide. Kreusler (Zeitsch. anal. Chem. 1885, 24, 453) uses sulphuric acid containing 200 grams of phosphorus pentoxide per litre.

Wilfarth (Chem. Zentr. [3] 16, 17, 113) finds that the oxidation of the organic matter takes place much more rapidly in presence of certain metallic oxides. Mercuric oxide is the most efficient, but cupric oxide answers almost equally well. The former produces mercuri-ammonium derivatives, which are not readily decomposed by caustic soda, and hence the alkaline liquid must be mixed with some potassium sulphide to decompose the mercury compounds The mercuric sulphide formed makes the liquid boil regularly without the addition of zinc. Ulsch recommends the use of ferrous sulphate instead of potassium sulphide; it may be added before the caustic soda.

Warington (Chem. News, 1885, 52, 162) removes nitrites and nitrates by boiling with ferrous sulphate and hydrochloric acid.

With a view to secure the reduction of nitro-derivatives, &c., and thus make the process generally applicable, Asboth (Chem. Zentr. [3] 17, 161) mixes 0·5 gram of the substance with 1 gram of pure sugar in the case of readily oxidisable compounds, and with 2 grams of benzoic acid in the case of nitrates and similar derivatives. Most probably the benzoic acid first forms nitro- derivatives, which are afterwards reduced. He adds Rochelle salt with the caustic soda in order to prevent precipitation of manganese, &c., and thus avoids bumping during distillation. With these modifications the method is applicable to all nitrogen compounds except those of the pyridine and quinoline series. E. Arnold (*ib.* p. 337) uses 0·5 gram of anhydrous cupric sulphate and 1 gram of metallic mercury in place of the oxides as recommended by Wilfarth, and heats 1 gram of the substance with these and 20 c.c of sulphuric acid containing 20–25 p.c. of phosphoric oxide.

C. Arnold (Arch. Pharm. [3] 24, 785) confirms Asboth's statements, but finds that in addition to pyridine and quinoline compounds, azo- derivatives and nitrites yield unsatisfactory results. He heats 0·5 gram of substance with 0·5 gram of anhydrous cupric sulphate, 1 gram of metallic mercury, 2 grams of phosphoric oxide, 1 gram of sugar, and in case of nitrates, &c., 2 grams of benzoic acid, and 20 c.c. of sulphuric acid.

Reitmair and Stutzer (Rep. Anal. Chem. 5, 232; Zeitsch. anal. Chem. 1886, 25, 582) use about 0·7 gram of mercuric oxide and 20 c.c of sulphuric acid, with a small fragment of paraffin in the case of substances rich in fat. They regard the use of phosphoric oxide as unnecessary, and the use of fuming sulphuric acid as undesirable on account of its liability to contain nitrogen oxides.

Jodlbauer (Chem. Zentr. [3] 17, 433) uses phenolsulphonic acid in place of benzoic acid, and reduces with zinc dust. He thus obtains good results even with nitrates. Reitmair and Stutzer (Rep. Anal. Chem. 7, 4) find that the nitrate must be somewhat finely divided; 0·5 to 1·0 gram of the substance is mixed with 50 c.c. of sulphuric acid containing 20 grams of phenol per litre, allowed to stand for a short time with occasional agitation, mixed with 2–3 grams of dry zinc powder and 1 or 2 drops of metallic mercury, and heated in the usual way. Conversion into ammonium sulphate requires one and a half hours.

A most important improvement in the Kjeldahl process due to Gunning (Zeitsch. anal. Chem. 28, 188), consists in the addition of potassium sulphate to the concentrated sulphuric acid. The solution of potassium hydrogen sulphate in concentrated sulphuric acid boils at a temperature considerably above the boiling-point of the strong acid and the oxidation of the organic matter is thereby greatly facilitated. Various oxidising and catalytic agents may be employed in conjunction with this mixture, and the following are among the many which have been suggested in addition to those already mentioned: platinic chloride, ferric chloride, manganese dioxide, magnesia, and sodium phosphate. The use of potassium permanganate has now been abandoned, and, in the case of refractory substances, oxidation is now generally induced by the catalytic action of mercury or its oxide. The following process is described by Dyer (Chem. Soc. Trans. 1895, 67, 811). The substance (0·5–5 grams) is introduced into a round-bottomed Jena flask, and heated gently with 20 c.c. of concentrated sulphuric acid containing a small globule of mercury. After the initial action has subsided, the temperature is raised to boiling, and in 15 minutes 10 grams of potassium sulphate are added, and the boiling continued till the solution is clear and colourless. The flask is closed with a loosely fitting bulb stopper, from the internal projection of which the condensed sulphuric acid drops back into the flask. There is, therefore, little loss of acid except through reduction to sulphurous acid. The product is rinsed into a capacious Jena distilling flask, rendered strongly alkaline with sodium hydroxide, with the addition of a small quantity of sodium sulphide, and the liquid distilled in a current of steam, the ammonia being collected and estimated in the usual way.

When nitrates are present, Jodlbauer's modification is employed, but the phenol may conveniently be replaced by salicylic acid. When the solution of this substance in concentrated sulphuric acid is poured quickly on to the weighed material, the loss due to the formation of lower oxides of nitrogen is avoided, and satisfactory results are obtained even when ammonium nitrate is present. This circumstance is of great importance in connection with the analysis of compound fertilisers containing both ammonium salts and alkali nitrates. Then zinc and mercury are added while the solution is still cold, and the former metal allowed to dissolve before the mixture is heated. Other reducing agents, such as sugar and sodium thiosulphate, may be used either alone or in conjunction with zinc. By the aid of this modified process satisfactory results are obtained in the analysis of organic nitro-, azo-, and hydrazo-derivatives. It has not been found possible to obtain correct estimations of nitrogen in sodium nitroprusside, phenylhydrazine and its derivatives, and in mixtures containing large proportions of chlorides and nitrates (*cf.* J. Amer. Chem. Soc. 17, 567; Analyst, 1905, 314; Ber. 1905, 38, 559; Chem. Soc. Proc. 1901, 25, 351; 1903, 27, 988).

The literature of nitrogen determinations is extremely voluminous. Summaries of contributions to this subject will be found in Zeitsch. anal. Chem. 1884, 23, 551; 24, 439; 25, 424 and 571; 26, 249; and Chem. News, 1888, 57, 62, *et seq.* In addition to the references already given, papers relating to Kjeldahl's process may be found in Zeitsch. anal. Chem. 24, 199, 388, and 393; 25, 149 and 155; 26, 92; 27, 222 and 398.

Chlorine, bromine, and iodine.

By lime. A tube about 40 cm. long and 7 mm. diameter, sealed at one end like a test-tube, is filled to a depth of 5 cm. with pure granulated quicklime. The substance is weighed into the tube and mixed with finely powdered lime by means of a copper wire twisted at the end like a corkscrew. The wire and tube are rinsed with lime, the tube is filled to within 5 cm. of the open end with granulated lime. The tube is gradually heated to redness from the front. When cold the contents of the tube are dissolved in water slightly acidified with nitric acid, filtered, and the halogen precipitated by silver nitrate.

In the case of iodine the substance is dissolved in water, filtered, mixed with silver nitrate, and finally acidified, in order to avoid liberation of iodine. A further precaution consists in adding a little sodium sulphite before each addition of nitric acid.

When the substance contains nitrogen, cyanides may be formed; but this is avoided by using pure soda-lime in place of lime. If the lime contains sulphates, some sulphide is liable to be produced. (On the preparation of pure lime, *see* Zeitsch. anal. Chem. 4, 51 and 15, 5.)

Liquids are contained in small bulbs with capillary openings, which are dropped into the tube before filling up with lime. The tube must be very gradually heated, and should be longer than usual.

Carius's method (Annalen, 1860, 116, 1; 1865, 136, 129; Ber. 1870, 3, 697). The substance is oxidised by heating with nitric acid in sealed tubes in presence of silver nitrate. In many cases acid of sp.gr. 1·2 and a temperature of 120°–200° will suffice; but substances which are more difficult to oxidise require acid of sp.gr. 1·42, mixed in special cases with some potassium dichromate, or the fuming acid of sp.gr. 1·5 may be used. If necessary the tubes may be heated as high as 300°. The quantity of acid used should not be more than twice that theoretically required for complete oxidation, and the tube must not contain more than 4 grams of nitric acid for each 50 c.c. of its volume. If the operation is prolonged, it is desirable to reduce the pressure in the tube by opening it from time to time by heating the capillary end of the previously cooled tube in a flame until it softens, when the gas forces its way out.

The weighed substance is enclosed in a narrow tube of thin glass of such length that its mouth projects above the nitric acid in the tube, and the acid does not come in contact with the substance until the tube is sealed. The tubes used should be about 15 mm. in diameter and 1·5–2 mm. thick in the glass. After introduction of the substance they are drawn out to a capillary tube with thick walls, which is then sealed. The sealed tubes are heated in a pressure tube furnace tilted at one end so that the capillary ends of the tubes do not come into contact with the liquid. After being heated, the tubes should on no account be removed from the protecting iron or steel tube until they have been opened. For this purpose the tubes are held in position by means of a cork collar through which the capillary ends project out of the furnace. The capillary end is first gently warmed to volatilise any condensed acid, and then heated more strongly until the gases under pressure blow a hole through the softened tip of the sealed capillary. In this operation the pressure of the imprisoned gases is very great, and it is extremely dangerous to attempt to open the tube with a file. The tube furnace should only be used for this purpose within a well-protected enclosure (Fig. 28), so as to minimise the personal risks arising from explosions of the heated tubes.

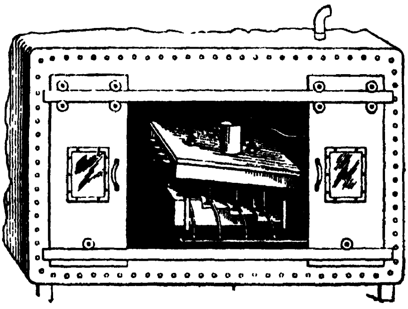


Fig. 28.

The silver salt formed is rinsed out of the opened tube and treated in the usual way.

For the estimation of iodine in organic compounds this method is to be preferred to the lime process, but as the silver nitrate and silver iodide frequently form a fused yellow mass, the mixture must be extracted thoroughly with hot water in order to remove the former salt. The silver halide obtained by the Carius method is collected in a tared Gooch crucible, washed successively with water and alcohol, dried at 100°, and weighed.

Stepanow's method. The substance is boiled with alcohol (20–40 c.c.) and sodium is added at such a rate that a vigorous reaction is maintained. A large excess of the metal is essential

$$XCl+2Na+C_2H_5{\cdot}OH=XH+NaCl+C_2H_5{\cdot}ONa.$$

When all the sodium has dissolved, 20–40 c.c. of water are added, and the alcohol removed by distillation. The aqueous solution is acidified with nitric acid, and the halogen estimated gravimetrically, or volumetrically by Volhard's method (Ber. 1906, 39, 4056; cf. Bacon, J. Amer. Chem. Soc. 1909, 31, 49). By using the latter method and weighing the mixed silver halides, the two halogens can be estimated indirectly in the same compound.

Pringsheim's method consists in burning the organic substance with sodium peroxide. Compounds containing more than 75 p.c. of carbon are mixed with 18 parts of this oxidising agent, and those with 50–75 p.c. of carbon with 16 parts. Substances containing less than 25 p.c. of carbon are mixed with sugar or naphthalene, and treated with 16–18 parts of the peroxide. The mixture is placed in a steel crucible surrounded by water and having a perforated lid through which a glowing iron wire is thrust to cause ignition. The product is extracted with water, acidified with nitric acid, and the halogen estimated in the usual way (Ber. 1903, 36, 4244; 1904, 37, 324; 1905, 38, 2459; Amer. Chem. J. 1904, 31, 386; *cf.* Moir, Chem. Soc. Proc. 1907, 23, 233; Baubigny, Bull. Soc. chim. 1908, (iv.) 3, 630).

Sulphur and phosphorus.

Non-volatile substances. Pure caustic potash is fused in a silver dish with about one-sixth its weight of potassium nitrate and a little water. When cold the substance is weighed into the dish, which is again heated, the substance being mixed with the alkali by means of a silver spatula. When oxidation is complete, the mass is allowed to cool, and is then dissolved in water acidified with hydrochloric acid, and the sulphuric or phosphoric acid estimated in the usual way.

Carius's method is carried out exactly as in the estimation of the halogens. Sulphur is oxidised to sulphuric acid and phosphorus to phosphoric acid. It is advisable to remove the greater part of the nitric acid before precipitating barium sulphate or magnesium ammonium phosphate.

Another method applicable to volatile and non-volatile substances is as follows:—Into a combustion tube 40 cm. long, sealed at one end, is introduced 2–3 grams of pure mercuric oxide, then a mixture of the substance with equal proportions of mercuric oxide and pure anhydrous sodium carbonate, and the remainder of the tube is filled with sodium carbonate mixed with a small quantity of mercuric oxide. The open end of the tube is closed by a cork carrying a glass tube dipping under water, in which the mercury is condensed. The tube is carefully heated so that the front layer of sodium carbonate is red hot before the substance begins to volatilise. The substance is then rapidly heated, so that decomposition is complete in about fifteen minutes, and finally the mercuric oxide at the rear end of the tube is heated until oxygen issues from the end of the delivery-tube (Russell, Chem. Soc. Trans. 1854, 7, 212; J. pr. Chem. 1855, 64, 230). The contents of the cooled tube are dissolved in water, a small quantity of bromine water added to oxidise any sulphide, the solution acidified with hydrochloric acid, boiled to expel bromine, and the sulphuric acid or phosphoric acid estimated in the usual way.

Many non-volatile substances may be oxidised by heating with pure concentrated caustic potash solution, diluting with twice the volume of water, and treating with a current of chlorine. After complete oxidation the solution is acidified, heated to expel chlorine, and the sulphuric or phosphoric acid determined.

Arsenic. The estimation of this element in organic compounds has recently acquired increased importance owing to the application of these substances in therapeutics. One of the earliest methods, due to La Coste and Michaelis (Annalen, 1880, 201, 224), consisted in mixing the substance with soda-lime, and heating the mixture in a stream of air or oxygen. The residue was dissolved in nitric or hydrochloric acid, the arsenic precipitated as sulphide, and afterwards converted into magnesium pyroarsenate. Monthoulé recommends destroying the organic matter with nitric acid containing magnesium nitrate, when a final ignition leads to the formation of magnesium arsenate (Ann. Chim. anal. 1904, 9, 308).

Pringsheim oxidises the organic arsenic derivative with sodium peroxide, and estimates the arsenic as magnesium pyroarsenate (Amer. Chem. J., 1904, 31, 386).

The following procedure has been shown to be applicable to the organic arsenical drugs now on the market. The substance (0·2–0·3 gram) is mixed with 10–15 grams of sodium peroxide and sodium carbonate in equal proportions, the mixture heated gently in a nickel crucible for 15 minutes, and the temperature then raised to dull redness for 5 minutes. The product is extracted with water, 25–31 c.c. of sulphuric acid (1 : 1) added, and the solution concentrated to 100 c.c., when 1 gram of potassium iodide is added and the liquid boiled down to 40 c.c. After destroying any trace of iodine with a few drops of sulphurous acid, the solution is diluted considerably with hot water, and the arsenic precipitated as sulphide. The precipitate, after washing three times with hot water, is dissolved with 20 c.c. of $N/2$-sodium hydroxide, and the filtered solution treated with 30 c.c. of hydrogen peroxide (20 vols.), the excess of this reagent being destroyed by heating on the water-bath. A few drops of phenolphthaleïn are added followed successively by 11 c.c. of sulphuric acid (1 : 1) and one gram of potassium iodide; the solution is evaporated down to 40 c.c. and the pale-yellow colour removed by sulphurous acid. Cold water is then added, and the diluted solution neutralised with $2N$-sodium hydroxide, and just acidified with sulphuric acid. The arsenite solution is now titrated with standard iodine solution and starch in the presence of sodium hydrogen carbonate or sodium phosphate (Little, Cahen, and Morgan, Chem. Soc. Trans. 1909, 95, 1477).

Antimony. When present in organic compounds, this element may be estimated by acidifying the product of the sodium peroxide fusion (*v. Arsenic, supra*), and precipitating as sulphide, this precipitate being collected, washed, and weighed in the manner indicated under *Gravimetric determinations.*

Oxygen. No satisfactory method has yet been devised for the direct determination of this element, and it is usually estimated by difference (*v.* v. Baumhauer, Annalen, 90, 228; Zeitsch. anal. Chem. 5, 141; Stromeyer, Annalen, 117, 217; Mitscherlich, Zeitsch. anal. Chem. 6, 136; 7, 272; 13, 74, and 15, 371; Ladenburg, Annalen, 135, 1; Maumené, Compt. rend. 55, 432; and Cretin, Zeitsch. anal. Chem. 13, 1).

Proximate analysis of carbon compounds. The methods to be adopted for the separation of the constituents of any particular mixture will depend entirely upon the nature of the mixture. It is only possible to describe the general methods which are found to be most useful in organic analysis. To a certain limited extent these operations are applicable to the proximate analysis of complex inorganic mixtures.

Fractional distillation is available for the separation of liquids which differ considerably in their boiling points (*v.* DISTILLATION).

Distillation in a current of steam is frequently employed as a method of proximate analysis. In this way volatile organic acids can be separated from volatile bases by steam-distilling the mixture in the presence of mineral acids. On the other hand, volatile bases are separated from organic acids by distilling in steam the mixture of these substances rendered alkaline by sodium or potassium hydroxide.

Fractional precipitation may be employed for the separation of substances, some of which are precipitated by a given reagent, whilst the others are not; or for the separation of substances which differ in the *order* of their precipitation. If, for example, silver nitrate is added in successive small quantities to a solution containing an iodide, bromide, and chloride, the first portion of the precipitate contains the greater part of the iodine; the middle portion contains the greater part of the bromine; and the last portion the greater part of the chlorine. In a similar manner organic acids can, not unfrequently, be separated by taking advantage of differences in the order of their precipitation by silver nitrate or lead acetate. In these cases the separated precipitates can be suspended in water and decomposed by hydrogen sulphide, when the acids are again liberated.

Fractional crystallisation may be adopted in the case of substances which differ in their solubility in one and the same solvent. The solution is concentrated somewhat, and the crystals which separate are removed; the mother liquor is still further concentrated, and the second crop of crystals is removed, this process being repeated as often as the case demands. The least soluble compound is mainly in the first crop of crystals; the most soluble is in the last mother liquor.

Fractional saturation is an analogous process, but is of more limited application. It was employed by Liebig for the separation of volatile organic acids. The mixture of acids is mixed with a quantity of caustic soda or potash insufficient for complete saturation, and is then distilled. The acids of higher molecular weight are first neutralised and converted into salts, which of course remain in the retort, whilst the acids of lower molecular weight are found in the free state in the distillate. Anything like complete separation is only to be obtained by many repetitions of this process.

Fractional solution.—The most useful and most generally applicable method of proximate analysis is based upon the different solubilities of various substances in different menstrua. The mixture is treated successively with various solvents, each of which dissolves some of the constituents, but leaves the others undissolved. Advantage may also be taken of the fact that the solubilities are in many cases modified by a rise of temperature. Further, if two substances differ considerably in their solubility in one and the same liquid, they may be separated by treatment with successive small quantities of the liquid, which removes the more soluble compound but leaves the greater part of the other undissolved. The following is a list of the solvents commonly employed, with indications as to their general properties:—

Water dissolves many salts and acids; inorganic and organic alkalis and their salts; carbohydrates, gums, certain alcohols, polyhydric phenols, and other highly oxidised carbon compounds which are not readily soluble in alcohol, ether, &c. On the other hand, it does not dissolve the carbonates, phosphates, oxalates, and certain other salts of the heavier metals. Very many organic substances are insoluble in this liquid. It decomposes the halogen compounds of the acid radicles and certain other compounds, and converts many normal metallic salts into basic salts, part of the acid passing into solution in the free state.

Dilute acids will dissolve many salts, and also some organic substances which are insoluble in water.

Alcohol dissolves many salts, caustic alkalis, hydrocarbons, fatty acids, resins, and a very large number of carbon compounds. It reacts with many haloid substitution derivatives, and hence is not a suitable solvent for this class of compounds.

Ether dissolves a few salts, and is an excellent solvent for hydrocarbons, fats, resins, alkaloids, and almost all organic compounds which are insoluble in water. It reacts with very few substances, and boils at a low temperature, so that it can readily be distilled off and the dissolved substance recovered.

Benzene dissolves iodine, sulphur, phosphorus, oils, fats, wax, camphor, resins, caoutchouc, gutta-percha, &c., and is especially useful as a solvent for haloid derivatives, on which it has no action. In certain instances this hydrocarbon may be replaced by its homologues, toluene, and the xylenes.

Carbon disulphide shares with ether the advantage of being readily volatile. It should always be purified from dissolved sulphur before being used. The best plan is to mix it with a small quantity of white wax, and then distil off the disulphide on a water-bath. It dissolves sulphur, phosphorus, iodine, fats, essential oils, resins, caoutchouc, &c.; but its solvent powers are comparatively limited, and almost all salts and very many carbon compounds are insoluble in it.

Light petroleum consists of the more volatile hydrocarbons of the paraffin series. It occurs in commerce in several varieties under different names. *Petroleum ether* boils at 50°–60°; *petroleum benzene*, at 70°–90°; *ligroïn*, at 90°–120°. They are excellent solvents for oils and fats, but dissolve very few other compounds. Three grades of light petroleum are now obtainable for use as solvents, boiling respectively at 40°–60°, 60°–80°, and 80°–100°.

Chloroform readily dissolves oils, fats, and similar substances, and is especially useful as a solvent for alkaloids.

The chloro- derivatives of ethane and ethylene have been introduced as useful non-inflammable solvents for oils, fats, or resins; these liquids give a wide range of boiling-points and solvent action (Koller, 7th Congress Applied Chemistry, 1909). A large number of other solvents are applied in certain special cases, and among those more commonly employed may be mentioned, acetone, ethyl acetate, amyl alcohol, pyridine, aniline, and nitrobenzene.

The treatment of a solid with a volatile solvent must be conducted in a special apparatus, especially if the liquid is to be heated. Various forms of apparatus have been devised for this purpose, but there is none more efficient than that of Soxhlet (Dingl. poly. J. 232, 461). It consists of a short wide test tube (E), open at the top but closed at the bottom, to which is sealed a narrower tube (N) which can be fitted into a small weighed flask by means of a cork. Communication between the two tubes is made by means of (1) a narrow side tube (*s*) which opens into the bottom of the wider upper tube, forms a siphon, and descends through the lower tube nearly to the bottom of the flask; and (2) a wider side tube (*t*) which enters the upper tube near the top and the lower tube near the junction (Fig. 29). A weighed quantity of the substance to be treated is placed in a cylinder of filter paper open at the top, and introduced into the upper tube, or the bottom of the tube is packed with purified cotton wool, and the substance is placed upon this. A quantity of the solvent rather more than sufficient to fill the upper tube to the level of the bend in the siphon, is placed in the flask and heated to boiling by means of a water-bath. The upper tube is attached to a reflux condenser, care being taken that the condensed liquid falls directly into the cylinder containing the substance. The vapour passes up the wide side tube, is condensed, falls upon the substance, and filters through the paper or cotton wool. As soon as the liquid rises to the bend of the siphon, the latter draws off the clear solution into the flask, and the liquid is again volatilised whilst the dissolved matter remains in the flask. The process goes on automatically, and the substance can be extracted many times with a small quantity of liquid. When extraction is complete, the flask is connected with an ordinary condenser, the liquid is distilled off, and the residue dried and weighed if necessary.

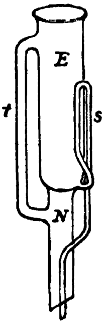


Fig. 29.

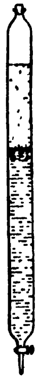


Fig. 30.

A convenient apparatus for treatment with solvents in dishes has been described by A. W. Blyth (Chem. Soc. Trans. 1880, 37, 140).

In many cases substances in solution can be removed and separated by agitating the liquid with some non-miscible solvent. The alkaloids and many amines can be removed from aqueous solutions by means of ether, whilst metallic salts are left; fatty substances can be removed from liquids by means of light petroleum, and so on. Extractions of this kind are best made in a separator consisting of a somewhat wide tube contracted at one end, which is fitted with a cork or stopper, whilst the other end is drawn out into a narrow tube provided either with a stop-cock or an indiarubber tube and a pinch-cock (Fig. 30). The liquid and the solvent can be completely mixed by agitation, and after they have separated the lower layer can be drawn off. If it is required to remove the supernatant liquid in this or any similar case, a somewhat narrow tube is bent twice at right angles, and one limb is fitted by means of a cork into a distilling or other flask, which is connected with an aspirator, whilst the other limb of the tube is placed in the liquid. When the aspirator is set in action, the liquid is drawn over into the flask, from which it can be distilled. With care a very accurate separation can be made, and the tube is readily rinsed by drawing some of the fresh solvent through it. This method may be rendered approximately quantitative by calibrating the above cylindrical separator (Fig. 30).

The microscope is of the greatest service in ascertaining whether a substance is a single compound or a mixture, and a microscopic examination of the various products obtained in the course of a proximate analysis affords valuable information as to the extent to which separation has been effected.

ESTIMATION OF RADICALS COMMONLY OCCURRING IN ORGANIC COMPOUNDS.

In this section it is only possible to indicate briefly a few of the most general methods by which certain typical radicals present in organic compounds can be estimated.

Hydroxyl. A known weight of the hydroxylic compound is treated with excess of magnesium methyl iodide (Grignard's reagent), and the amount of methane evolved is measured in a gas burette (Fig. 31).

$$R\cdot OH+CH_3\cdot MgI=R\cdot OMgI+CH_4.$$

The organic magnesium compound is dissolved in dry amyl ether or phenetole, and if the hydroxylic compound is too insoluble in either of these solvents, it may be dissolved in dry pyridine. (Hibbert and Sudborough, Chem. Soc. Trans. 1904, 85, 933; and Zerewitinoff, Ber. 1907, 40, 2023.)

This process has been extended to the estimation of sulphydryl- (SH), imino-, and amino- groups, and for all active hydrogen atoms (cf. Ber. 1908, 41, 2233 and 3025).

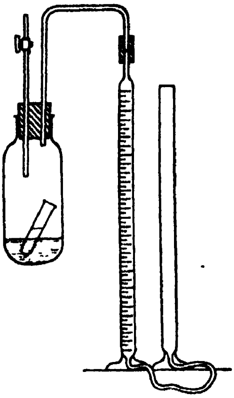


Fig. 31.

Methoxyl.

The estimation of methoxyl, a radical present in many naturally occurring organic compounds, is generally accomplished by Zeisel's method, which consists in heating the substance with concentrated hydriodic acid or with a mixture of this acid and acetic anhydride. Methyl iodide is evolved and absorbed in alcoholic silver nitrate, with the result that silver iodide is precipitated, each molecular proportion of this substance being equivalent to one methoxyl group. Zeisel's original apparatus (Monatsh. 1885, 6, 989; 1886, 7, 406) has been modified subsequently by several investigators (M. Bamberger, Monatsh. 1894, 15, 904; Perkin, Chem Soc. Trans. 1903, 83, 1367; Hesse, Ber. 1906, 39, 1142; Decher, Ber. 1903, 36, 2895; Hewitt and Moore, Chem. Soc. Trans. 1902, 81, 318). Of these modifications Perkin's (Fig. 32) is probably the simplest; it consists of a distilling flask, A, with a very long neck (20–25 cm.) heated in a glycerine bath at 130°–140°, a current of carbon dioxide being passed through the mixture of substance and concentrated hydriodic acid. The heating is continued for one hour, and the temperature finally raised, so that the hydriodic acid boils gently, but without distilling into the side tube of the distilling flask. The methyl iodide is collected in two flasks, B, containing alcoholic silver nitrate. The precipitated silver iodide is treated with nitric acid, the alcohol evaporated, and the precipitate collected and weighed in the usual manner.

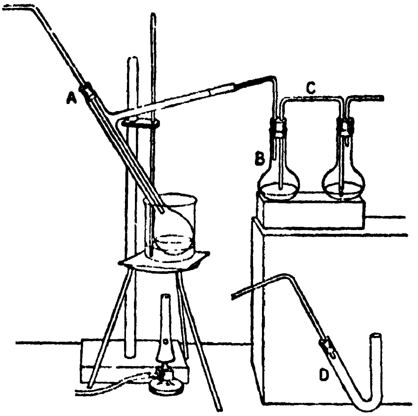


Fig. 32.

Hewitt and Jones (Chem. Soc. Trans. 1919, 115, 193) combine the methyl iodide with pyridine, thus obtaining the iodide in an ionisable form whereby it can be estimated volumetrically. The pyridine and its methiodide are diluted with water, acidified with nitric acid, a known amount of silver nitrate added, and the excess of the latter determined by thiocyanate according to Volhard's method.

Zeisel's method and its modifications are applicable to the estimation of ethoxyl, but the results obtained are generally less accurate.

Methyl.

A further modification of Zeisel's method renders it available for the estimation of methyl groups attached to nitrogen. The substance is heated with concentrated hydriodic acid and dry ammonium iodide, and the methyl iodide evolved dealt with in the manner indicated above (Herzig and H. Meyer, Ber. 1894, 37, 319; Monatsh. 1894, 15, 613; 1895, 16, 599; 1897, 18, 379; Kirpal, Ber. 1908, 41, 820).

Acetyl.

It is only possible in comparatively few cases to determine with certainty by ultimate analysis the number of acetyl groups existing in organic compounds. For example, the mono-, di-, and tri- acetyl derivatives of the trihydroxybenzenes have approximately the same percentage composition. These and other similar acetyl derivates are hydrolysable by standard caustic alkalis employed in alcoholic solutions, even when they are not readily attacked in aqueous solutions (Benedikt and Ulzer, Monatsh. 1887, 8, 41; Van Romburgh, Rec. trav. chim. 1882, 1, 48; R. Meyer and Hartmann, Ber. 1905, 38, 3956). Acid hydrolysis may be employed in a large number of cases and the volatile acetic acid distilled into standard alkali, the excess of which is determined by alkalimetry. According to Wenzel's process, the acetyl derivative is first hydrolysed by moderately strong sulphuric acid (1 : $2H_2O$), and the mixture treated with monosodium phosphate and boiled down to dryness; the sulphuric acid is fixed as sodium sulphate, and the acetic acid is distilled into a known excess of standard alkali, the distillation being carried out under reduced pressure (Monatsh. 1893, 14, 478; 1897, 18, 659).

The destructive action of strong sulphuric acid on organic compounds may be avoided by the use of the aromatic sulphonic acids as hydrolytic agents. The acetyl compound is distilled in steam in a 10 p.c. solution of benzenesulphonic acid or one of the naphthalenesulphonic acids; the distillate, which contains all the acetic acid furnished by the hydrolysis, is titrated with standard barium hydroxide (Sudborough and Thomas, Chem. Soc. Trans. 1905, 87, 1752).

A. G. Perkin hydrolyses the acetyl compound with alcoholic sulphuric acid, adding fresh alcohol from time to time. The ethyl acetate obtained in the distillate is then hydrolysed with a known amount of standard caustic alkali, and the excess of the latter ascertained with standard acid (Chem. Soc. Trans. 1904, 85, 1462; 1905, 87, 107; 1907, 91, 1230)

Carboxyl.

In many cases the number of carboxyl (CO_2H) groups in an organic compound can be determined by the analysis of its neutral salts. For this purpose the silver salts are generally selected, as they are usually anhydrous, and indicate the normal basicity of the organic acid. The aromatic hydroxy-carboxylic acids (*e.g.* 1 : 5-dinitro-*p*-hydroxybenzoic acid) take up two atoms of silver, one replacing the carboxylic, and the other the phenolic hydrogen. Some silver salts of organic acids are sensitive to light, and others are very explosive. The more stable ones can be analysed by direct ignition and weighing the residual silver. In other cases the organic matter must be destroyed with nitric acid, and the silver estimated as chloride in the acid liquid.

Other metallic salts are frequently employed in determining the basicity of carboxylic acids, and it is advisable before arriving at a final conclusion to estimate the metals in a series of these compounds.

If the molecular weight of a carboxylic acid is known, the basicity can often be determined by titration with aqueous or alcoholic sodium, potassium, or barium hydroxide; the indicators generally employed are phenolphthaleïn, methyl orange, and lacmoid.

The following indirect method has been recommended (P. C. McIlhiney, Amer. Chem. J. 1894, 16, 408) for the estimation of carboxyl groups. The substance (1 gram) is dissolved in excess of alcoholic potash, the alcohol being at least 93 p.c. The solution is saturated with carbon dioxide until the excess of alkali is precipitated as carbonate or bicarbonate. The precipitate is collected and washed with alcohol, the filtrate is distilled to remove the solvent, and the residue containing the potassium salt of the organic acid is distilled with 10 p.c. aqueous ammonium chloride, the ammonia evolved being estimated in the usual way. Each molecular proportion of ammonia corresponds with one carboxyl group. This method is applicable to the weaker fatty acids.

Carboxyl can be estimated by a method based on the following reaction:—

$$6R{\cdot}CO_2H+5KI+KIO_3=6R{\cdot}CO_2K+3I_2+3H_2O$$

The weighed substance is digested for 12 hours with an aqueous solution of pure potassium iodide and iodate in a stoppered vessel. The mixture containing the liberated iodine is rinsed unto the generating vessel of a gas volumeter and treated with alkaline hydrogen peroxide, when the oxygen evolved

$$I_2+2KOH+H_2O_2=2KI+2H_2O+O_2$$

is a measure of the carboxyl groups originally present ($6CO_2H \equiv 3O_2$) (Baumann-Kux, Zeitsch. anal. Chem. 1893, 32, 129; Annalen, 1904, 335, 4; *cf.* Gröger, Zeitsch. angew. Chem. 1890, 3, 353, 385). It should be noticed that acidic substances not containing carboxyl groups (*e.g.* picric acid) liberate iodine from the iodide-iodate mixture.

Carbonyl.

The carbonyl group, whether present in aldehydes $R{\cdot}CO{\cdot}H$ or ketones $R{\cdot}CO{\cdot}R'$, can be detected by means of the following colour-reaction. An aqueous or alcoholic solution of the substance is treated with a 0·5 to 1 p.c. solution of the hydrochloride of an aromatic meta-diamine (meta-phenylenediamine or its homologues), when in a few minutes an intense green fluorescence is developed, which attains its maximum intensity after two hours. All aldehydes give this reaction, but the mixed ketones and ketonic acids do not (Windisch. Zeitsch. anal. Chem. 1888, 27, 514).

Practically all aldehydes restore the colour to the following solution (Schiff's reagent). A litre of 0·10 p.c. magenta solution is decolourised by adding 20 c.c. of sodium bisulphite solution (30°Bé.) followed after one hour by 10 c.c. of concentrated hydrochloric acid. (For the exceptions, *cf.* Bittó, Zeitsch. anal. Chem. 1897, 36, 375.) The reaction has also been utilised quantitatively (McKay Chase, J. Amer. Chem. Soc. 1906, 28, 1472; Schimmel & Co., Ber. 1907, 123).

Phenylhydrazine condenses with aldehydes and ketones, yielding phenylhydrazones. When the mixture is treated with Fehling's solution (70 grams $CuSO_4,5H_2O$, 350 grams Rochelle salt, and 260 grams KOH, in 2 litres), the excess of phenylhydrazine is decomposed, evolving nitrogen:

$$C_6H_5{\cdot}NH{\cdot}NH_2+O=C_6H_6+H_2O+N_2,$$

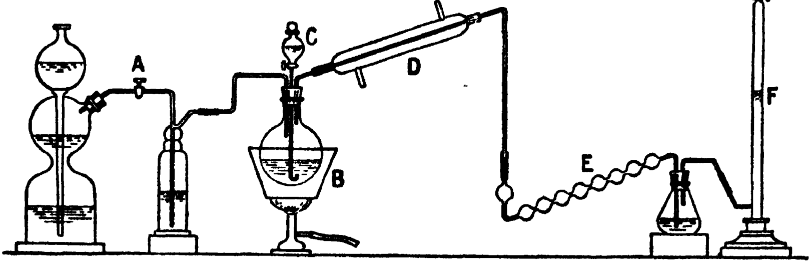


FIG. 33.

while the phenylhydrazone remains unchanged. The estimation is carried out in a flask, B, connected with a carbon dioxide generator, A (Fig. 33). A known volume of Barreswil's solution is introduced and covered with a layer of petroleum to prevent the caustic potash from absorbing the carbon dioxide. A blank experiment is first made with the standard solution of phenylhydrazine hydrochloride and aqueous sodium acetate, the nitrogen evolved on heating the solutions together being collected in a Schiff's nitrometer, F. The experiment is then repeated with the same solutions of phenylhydrazine and sodium acetate *plus* the carbonyl compound; the difference between the two volumes of nitrogen collected is a measure of the carbonyl present in the compound (Strache, Monatsh. 1891, 12, 524; 1892, 13, 299; 1893, 14, 270; Watson Smith, Chem. News, 1906, 93, 83).

When the carbonyl compound (*e.g.* pyruvic acid) condenses readily with phenylhydrazine or its hydrochloride in aqueous solution, the excess of this base can be estimated by adding excess of *N*/10-iodine solution, and titrating the remaining iodine with standard sulphurous acid or thiosulphate, using starch as indicator. This estimation is based on the following reaction:—

$$C_6H_5\cdot NH\cdot NH_2+2I_2=3HI+C_6H_5I+N_2.$$

The phenylhydrazone is not affected by the iodine solution (E. v. Meyer, J. pr. Chem. 1887, [2] 36, 115; *cf.* Petrenko-Kritschenko, Ber. 1901, 34, 1699; and Annalen, 1905, 341, 15, 150).

Organic amines.

The organic amines are divisible into three classes, primary, secondary, and tertiary, containing their nitrogen atoms combined respectively with one, two, and three organic groups. These groups may be either aliphatic or aromatic, and the reactions of each of the three classes of amines depend very largely on the nature of the organic groups to which the basic nitrogen atom is attached.

Primary amines. The primary amino-group $C\cdot NH_2$ may be detected by the carbylamine reaction (Hofmann, Ber. 1870, 3, 767), irrespective of the nature of the organic group, which may be either aliphatic, aromatic, or hydroaromatic (*cf.* Monatsh. 1896, 17, 397). The test consists in warming the substance in alcoholic solution with chloroform and caustic potash, when a carbylamine (iso-nitrile) is produced, which has a pungent disagreeable odour:

$$R\cdot HN_2+CHCl_3+3KOH=R\cdot NC+3KCl+3H_2O.$$

The primary amines all interact with nitrous acid, but the aliphatic bases are immediately converted into hydroxyl derivatives (alcohols), whereas the aromatic bases furnish diazo-derivatives from which the nitrogen is evolved rapidly on warming or slowly at the ordinary temperature.

In the case of the aliphatic primary amines, this nitrogen can be collected, and the amount indicates the proportion of amino- groups present. As nitrous acid itself decomposes readily, evolving oxides of nitrogen, Staněk recommends the use of nitrosyl chloride, obtained by adding fuming hydrochloric acid to 40 p.c. aqueous sodium nitrite (Zeitsch. physiol. Chem. 1905, 46, 263). This reagent can be mixed with saturated salt solution without undergoing decomposition; the aliphatic amino-carboxylic acids (glycine, &c.) can be readily decomposed by it in a current of carbon dioxide, and the nitrogen evolved is freed from the former gas and traces of oxides of nitrogen by passing the mixed gases through alkaline permanganate solution. Half the nitrogen measured in the gas burette corresponds with that originally present in the amino-acid.

In the case of the aromatic primary amines, the acid solution of the base is carefully diazotised at 0° with standard sodium nitrite; the end-point is reached when a drop of the solution gives a blue colour on starch-iodide paper. The sodium nitrite solution may be standardised with either potassium permanganate, sodium sulphanilate $(NH_2\cdot C_6H_4\cdot SO_3Na,2H_2O)$ or para-toluidine (*cf.* Green and Rideal, Chem. News, 1884, 49, 173; Kinnicutt and Nef, Amer. Chem. J. 1886, 5, 388; Zeitsch. anal. Chem. 1886, 25, 223).

Estimation of imino-groups in secondary amines. A weighed quantity of the substance is mixed with a known excess of acetic anhydride, either alone or diluted with dry xylene or dimethylaniline (Bull. Soc. chim. 1892, [3] 7, 142; Chem. Zeit. 1893, 17, 27, 465). After one hour, water is added and the mixture warmed under a reflux apparatus, so that no anhydride is lost by evaporation. The solution is then titrated with standard barium hydroxide and phenolphthaleïn indicator. The amount of acetic acid present indicates the excess of acetic anhydride left over from the acetylation of the secondary base.

The tertiary amines and the quaternary ammonium salts do not give the reactions of the primary and secondary amines, but the total amount of basic nitrogen present in an organic amine can frequently be ascertained by the analysis of the characteristic salts of the base. The aurichlorides and platinichlorides may frequently be employed for this purpose, as these double salts on ignition leave a residue of the metal, each atomic proportion of gold corresponding to one basic nitrogen atom, while a similar quantity of platinum corresponds with two basic nitrogen atoms. In the majority of cases these double salts have respectively the general formulæ, $RHCl,AuCl_3$ and $(RHCl)_2PtCl_4$, and are obtained in the anhydrous condition; yet, in certain instances, hydrated forms are known and sometimes the salts themselves have an anomalous composition not corresponding with the general formulæ. Evidence obtained in this way should, if possible, be supplemented by the analysis of other salts, and for this purpose the ferrichlorides, chromates, oxalates, thiocyanates, ferrocyanides, picrates, and picrolonates have been employed, as well as the commoner nitrates, sulphates, and halide salts.

Gas analysis.

The experiments of Gay-Lussac established long ago the value, from a scientific point of view, of the determination of the volumetric composition of gases and the products formed by their interaction; but it is only within recent times that the methods of gas analysis have been applied to any great extent for technical purposes. The value of such determinations is now generally recognised on account of the information which they give respecting the efficiency of combustion, the progress of operations in which gases are consumed or produced, and the like.

With few exceptions the volumetric and not the gravimetric composition of the gas is required, and the measurements are essentially measurements of volumes. The gas to be examined is confined over mercury or water in a suitable measuring apparatus, and its composition is determined (1) by treatment with appropriate absorbing reagents and measurement of the contraction produced; (2) by exploding with oxygen or hydrogen and measuring the contraction; (3) by exploding with oxygen or hydrogen, measuring the contraction, and then treating with absorbing reagents, and measuring the second contraction. Sulphur dioxide and some other gases soluble in water are estimated by titration, a definite volume of the gas being drawn through a measured quantity of a standard solution, the excess of which is afterwards determined.

The highly refined and accurate methods of gas analysis employed for purposes of research are of little value for technical purposes on account of the length of time required for their execution. Information respecting these methods may be found in Bunsen's Gasometrische Methoden, 2nd ed. 1887; Sutton's Volumetric Analysis, 9th ed. 1904; Dittmar's Exercises in Quantitative Analysis, 1887; Hempel's Gasanalytische Methoden, 3rd ed. 1900; Travers' Experimental Study of Gases, 1901; *v.* also Thomas (Chem. Soc. Trans. 1879, 35, 213), and Meyer and Seubert (Chem. Soc. Trans. 1884, 45, 581). In this article only those methods will be described which are available for technical purposes.

Measurements.—The volume which a given mass of gas occupies depends on the temperature, the pressure, and the proportion of moisture which it contains. The temperature is ascertained by means of a thermometer attached to or suspended near to the measuring vessel. Measurements are usually made under atmospheric pressure, and this is determined by means of a barometer placed in the room in which the analysis is made. The siphon barometer is a convenient form of instrument for the purpose, and should stand on the table close to the gas apparatus. In case the level of the mercury or water in the measuring tube is higher than that in the trough or the attached tube, the true pressure upon the gas is given by the height of the barometer *minus* the difference between the mercury level inside and outside the tube. If water is used, the height of the water column divided by 13·6 gives the height of the corresponding column of mercury with sufficient accuracy. It is better to eliminate this correction by adjusting the liquid so that it is at the same level both inside and outside the tube, which is easily done.

The gas must be either perfectly dry or saturated with moisture. If an indefinite quantity of water vapour is present, accurate measurements are impossible. It is more convenient to measure the gas when moist, and hence if the gas is confined over mercury a few drops of water are introduced when the tube is filled with the mercury and this water is taken up by the gas. Under these conditions the surrounding pressure is balanced partly by the gas and partly by the aqueous vapour which it contains, and in order to ascertain the pressure which the gas itself is under, the tension of aqueous vapour at the particular temperature must be subtracted from the height of the barometer. The formula for reducing the volume of gas to the standard temperature and pressure (0° and 760 mm.) is:

$$V_0 = \frac{V + 273 \times (B - f)}{(273 + t) \times 760} \text{ or } V_0 = \frac{V \times (B - f)}{(1 + 0{\cdot}00366t \times 760)}.$$

in which V is the actual reading; *t*, the temperature; *f*, the tension of aqueous vapour at the temperature, *t*, and B, the height of the barometer. The reduction of the height of the barometer to 0° is necessary for accurate calculation, but may usually be omitted. The following table, abbreviated from Bunsen's Gasometrische Methoden, gives the value of 1+0·00366*t* for the ordinary range of temperature:—

t°	Number	Log	*t*°	Number	Log	*t*°	Number	Log
0°	1·00000	0·00000	11°	1·04026	0·01714	21°	1·07686	0·03216
1	1·00366	0·00159	12	1·04392	0·01867	22	1·08052	0·03363
2	1·00732	0·00317	13	1·04758	0·02019	23	1·08418	0·03510
3	1·01098	0·00474	14	1·05124	0·02170	24	1·08784	0·03656
4	1·01464	0·00631	15	1·05490	0·02321	25	1·09150	0·03802
5	1·01830	0·00788	16	1·05856	0·02471	26	1·09516	0·03948
6	1·02196	0·00943	17	1·06222	0·02621	27	1·09882	0·04093
7	1·02562	0·01099	18	1·06588	0·02771	28	1·10248	0·04237
8	1·02928	0·01253	19	1·06954	0·02921	29	1·10614	0·04381
9	1·03294	0·01407	20	1·07320	0·03068	30	1·10980	0·04524
10	1·03660	0·01561						

When the estimations are made rapidly, and only approximate results are required, the corrections for temperature and pressure are omitted, since it may be assumed that they remain constant during the analysis.

The following plan, described by Winkler, renders the use of the barometer and thermometer unnecessary, and makes the calculation much simpler. It is an adaptation of Williamson and Russell's method of always measuring the volume of the gas at the same degree of elasticity. A tube about 1 metre long, closed at one end and graduated to 120° c.c. in tenths is moistened internally with a few drops of water, and mercury is poured in in such quantity that when the tube is inverted the mercury stands somewhat higher than 100. The volume which 100 c.c. of air measured at standard temperature and pressure should occupy under the conditions described, is calculated from the expression:

$$V = \frac{(760-4{\cdot}5)100\times(278+t)}{278(B-f)} \text{ or } \frac{(760-4{\cdot}5)100\times1+0{\cdot}00866t)}{B-f}$$

and air is carefully introduced into the tube until, when the mercury is at the same level inside and outside the tube, it stands exactly at the calculated volume. The tube now contains a quantity of gas saturated with moisture, which, under standard conditions, would occupy 100 c.c., but its actual volume varies in the same ratio as the volume of gas to be measured. The two tubes are allowed to stand side by side, and when the levels have been properly adjusted in each case the volume of the gas to be measured and the volume of the air in the comparison tube are read off. The volume (under standard conditions) of the gas under examination is obtained by the proportion

$$V : V_0 : : V_1' : V_0',$$

in which V is the actual volume of air in the comparison-tube; V_0, its volume under standard conditions, which is always 100; V_1', the observed volume of the gas to be measured; and V_0', its volume under standard conditions.

During the operations the temperature should be kept as constant as possible, and the readings should be taken rapidly, otherwise the proximity of the body will cause variations in the temperature of the gas. It is an advantage to have the measuring tube surrounded by a wider tube which is filled with water. The most accurate method is to take the readings through a carefully levelled telescope (a cathetometer) at a distance of about five or six feet. This also avoids parallax. The measuring tube must be kept vertical, and when water is the confining liquid, sufficient time must be given for the liquid to run down the sides of the tube. Not unfrequently this requires several minutes.

Reagents.

All liquid reagents should be saturated with the gases which they do not absorb chemically. It is desirable that the tensions of these gases in the liquids should be approximately equal to their tensions in the gases which are to be analysed, in order to avoid exchanges between the gas and the absorbing liquid. This is best secured by going through the process two or three times without making measurements, whenever the pipettes have been freshly filled. Liquids used for the analysis of, say, flue gases, should not be used for gases of a different character, *i.e.* which contain the constituents in very different proportions.

Bromine water is used for absorbing olefines. It should be well saturated with bromine and kept in the dark.

Cuprous chloride is made by dissolving 50 grams of cupric oxide in hydrochloric acid, adding 50 grams of copper, and boiling for some time with as little exposure to air as possible. The solution is then diluted to 1000 c.c. with hydrochloric acid of sp.gr. 1·12, and allowed to remain in contact with metallic copper in a closed vessel until the solution becomes colourless. This solution attacks mercury rapidly.

Cuproso-ammonium chloride, obtained by dissolving cuprous chloride in ammonia, does not attack mercury.

The stock solution is made by dissolving 200 grams of cuprous chloride and 250 grams of ammonium chloride in 750 c.c. of water; it is kept in stoppered bottles, and, when required, mixed with one-third its volume of ammonia solution (sp.gr. 0·91).

Hydrogen is obtained by the action of dilute sulphuric acid on pure zinc. The granulated zinc may be placed in a small bottle fitted with a capillary delivery tube, which can be closed by a tap or pinch-cock. The bottle has a tubulus at the bottom, and is connected by a caoutchouc tube with a similar bottle containing dilute sulphuric acid. The latter bottle is raised so that the acid runs on the zinc, and the action is allowed to proceed until the air is completely expelled from the first bottle. The tap is then closed, and the acid is driven back into the second bottle by the pressure of the hydrogen. It is advisable to keep the second bottle at a slightly higher level than the first, to avoid any chance of air leaking in. One of Hempel's tubulated absorption bulbs answers admirably (Fig. 41). The zinc is attached to a cork, which is inserted in the tubulus of the first bulb, and the acid is introduced. When all air is expelled, the capillary tube is closed, and the acid is driven up into the second bulb, so that the pipette is always charged with hydrogen under pressure.

Oxygen is obtained in a pure state by heating potassium chloride *without* manganese dioxide. The powdered chlorate is contained in a glass bulb, the neck of which is drawn out to form a narrow delivery tube.

Phosphorus is employed in the form of narrow sticks, which are made by melting it under warm water and drawing it up into narrow glass tubes. The upper ends of the tubes are closed by the finger, and they are plunged into cold water, when the phosphorus solidifies. It may also be used in a granular form, obtained by shaking the phosphorus vigorously with warm water in a well-closed flask until it solidifies.

Caustic potash (*or soda*) for Orsat's apparatus is dissolved in three parts of water, and the solution kept in well-stoppered bottles. Hempel uses a solution of caustic potash in two parts of water, which will absorb forty times its volume of carbon dioxide. It may, however, be used somewhat more dilute, and is then less liable to attack the glass.

Pyrogallol is kept in the solid state, and only dissolved immediately before being used. Orsat recommends a solution of 25 grams of pyrogallol in a small quantity of hot water, mixed with 150 c.c. of a solution of 1 part of caustic soda in 3 parts of water. Hempel uses a mixture of 25 c.c. of a 20 p.c. solution of pyrogallol with 75 c.c. of 33·3 p.c. caustic potash solution. This quantity will absorb 200 c.c. of oxygen.

Shipley (J. Amer. Chem. Soc. 1916, 38, 1687) found the most effective solution was prepared by adding 40 c.c. of water to 100 grams pyrogallol and adding 100 c.c. of 49 p.c. sodium hydroxide solution. No carbon monoxide is evolved from a solution of this strength.

Anderson (J. Ind. and Eng. Chem 1915, 7, 587) recommends a solution of 15 grams pyrogallol in 100 c.c. potassium hydroxide solution of sp.gr. 1·55.

Sulphuric acid of sp.gr. 1·84 is used as a drying agent and for the absorption of nitrogen oxides. Acid of the same strength mixed with so much sulphuric anhydride that it remains liquid at the ordinary temperature but solidifies if cooled, is used for absorbing ethylene and other hydrocarbons.

Water, which is very largely used for confining the gases, should be well saturated with air, but should not contain carbon dioxide. Distilled water is preferable, but any potable water of good quality may be used.

Standard solutions used in the estimation of gases by titration are known as *normal gas solutions* when they are of such strength that 1 c.c. of the solution is equivalent to 1 c.c. of the gas under standard conditions. A normal gas solution of iodine for the estimation of sulphur dioxide would contain 11·333 grams of iodine per litre, and the thiosulphate solution used in conjunction with it would be of equivalent strength.

In many cases it is the weight of the absorbed constituent per cubic metre or cubic foot of gas that is required, and the ordinary standard solutions may be used.

Methods of estimation.

Ammonia, by titration.

Benzene, by absorption in fuming nitric acid boiling at 86°, the nitrogen oxides being then removed by caustic potash. Fuming nitric acid also absorbs carbon dioxide and carbon monoxide. Like the olefines, benzene is absorbed by fuming sulphuric acid and by bromine water, and in fact no absorption method is at present known by means of which benzene and the olefines can be separated (Ber. 1888, 21, 3131).

Carbon dioxide, by absorption in potassium or sodium hydroxide.

Carbon monoxide, by absorption in a saturated solution of cuprous chloride in hydrochloric acid or ammonia. It seems (Ber. 1887, 20, 2754) that these solutions are liable to give off part of the dissolved carbon monoxide, especially after they have been used repeatedly. The error is less with the ammoniacal solution, and is reduced if the solution remains in contact with the gas for some time. The cuprous chloride solution should always be tolerably fresh, and should be saturated with hydrogen, nitrogen, and the other gases which usually occur with carbonic oxide (Ber. 1888, 21, 898). If the amount of carbon monoxide is small, it should be converted by combustion (*v. Hydrogen*) into carbon dioxide, which is afterwards absorbed by caustic potash. If the amount of carbon monoxide is large, the greater part may be absorbed by cuprous chloride, and the remainder removed by combustion and absorption.

The estimation of small quantities of carbon monoxide in air or other comparatively inert gases can be effected by passing the dried gas over solid iodine pentoxide. At temperatures varying from 40°–150° the following reaction occurs: $I_2O_5+5CO=5CO_2+I_2$. Either of the volatile products can be estimated: the iodine volumetrically by standard thiosulphate, or gravimetrically by absorption in a weighed tube containing copper powder; the carbon dioxide may be absorbed in standard barium hydroxide, and the excess of the latter titrated with oxalic acid. If carbon dioxide is present in the gas under examination, it is first removed by potassium or barium hydroxide. Below 60° no hydrocarbon except acetylene reduces iodic anhydride. At higher temperatures several unsaturated hydrocarbons have an appreciable action. Ethylene hinders the oxidation of carbon monoxide by the iodine pentoxide. The process is applicable to air containing one part of carbon monoxide in 30,000, and is used for estimating the monoxide occluded in steel (Gautier, Compt. rend. 1898, 126, 871, 1299; Jean, *ibid.* 1902, 135, 746; J. Amer. Chem. Soc. 1900, 22, 14; 1907, 29, 1589; Ann. Chim. anal. 1910, 15, 1).

Hydrogen is converted into water by combustion with air or oxygen, and the volume of the hydrogen is represented by two-thirds of the contraction consequent upon combustion. If the gas is confined over mercury, an excess of pure oxygen is introduced, the volume read off, and the pressure on the gas reduced considerably below atmospheric pressure by lowering the mercury in the level tube. The lower end of the explosion tube is closed, and combination is initiated by passing a spark from a coil between the platinum wires which are fused into the tube. The pressure is restored to the normal, and when the gas has cooled the volume is again read off.

When the gas is confined over water it is almost impossible to obtain satisfactory combustion, and it is much more convenient to pass the combustible mixture over gently heated spongy palladium. This is prepared by dissolving about two grams of palladium chloride in a small quantity of water, adding a small quantity of a saturated solution of sodium formate and sodium carbonate until the reaction is alkaline. About 1 gram of long and very soft asbestos fibres is introduced, and the pasty mass is dried at a gentle heat. In this way the asbestos is obtained covered with very finely divided palladium. After being completely dried at 100°, it is carefully washed with water

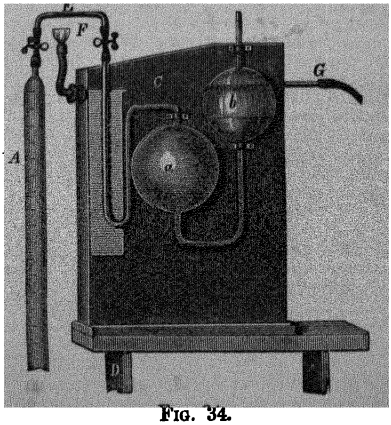


FIG. 34.

to remove soluble salts and again dried. Some of the fibres are moistened and twisted into a thread about 1 cm. long, which is then introduced into the middle of a stout capillary tube, B, about 15 cm. long and 1 mm. internal diameter, and this tube is bent at a right angle at each end, or in any other way convenient for its attachment to the measuring apparatus containing the gas. One end of the capillary is in communication with the graduated tube, A, and the other with a bulb pipette, C, filled completely with water, into which the gas is passed. A small gas or spirit-lamp flame is arranged to heat that part of the capillary which contains the asbestos. When the other gases have been estimated, the mixture of hydrogen and nitrogen which remain is mixed with air by lowering the level-vessel until the pressure is sufficiently reduced, and then putting the measuring tube in communication with the air. The stop-cock is then closed, the asbestos very gently heated, and the gas passed slowly through the capillary into the bulb and back again three or four times. When combustion is complete, the volume of the residual gas is measured.

This method may be employed in estimating hydrogen in the presence of methane, since the latter is not burnt under these conditions, providing that the temperature does not exceed 500° (J. Soc. Chem. Ind. 1903, 22, 925; 1905, 24, 1202; Zeitsch. angew. Chem. 1903, 16, 695).

The palladinised asbestos can be used in promoting the combustion of carbon monoxide.

Drehschmidt (Ber. 1888, 21, 3245) prefers a platinum tube 20 cm. long and 2 mm. thick, with a bore 0·7 mm. diameter. The bore is almost closed by the insertion of a palladium wire extending through the whole length of the tube. The tube is attached to a burette and an absorption pipette in the same manner as the glass tube; 5 to 6 cm. are heated to redness by means of a gas flame, and the gas is passed backwards and forwards until there is no further alteration of volume. No explosions occur even with mixtures of hydrogen and oxygen containing only a slight excess of the latter.

Hempel has applied the well-known absorption of hydrogen by palladium to the estimation of this gas. Pure palladium is indifferent towards hydrogen in the presence of methane and nitrogen, but when it contains a little palladious oxide combustion of some of the hydrogen occurs, and the heat generated ensures the absorption of the remainder. Palladium sponge is heated and allowed to cool slowly so that it becomes superficially oxidised. A U-tube of 4 mm. internal diameter and 20 cm. total length is charged with 4 grams of this oxidised sponge and maintained at 90°–100° by immersion in a beaker of hot water; this tube is interposed between the gas burette and a pipette filled with water. The absorption is effected by siphoning the gas backwards and forwards through the palladium sponge.

Hydrogen chloride, by titration.

Hydrogen sulphide, by titration.

Hydrocarbons other than olefines are estimated by combustion, preferably with oxygen over mercury under reduced pressure. Acetylene and benzene may be burnt over palladium, but require a somewhat high temperature. Methane cannot be burnt in this way even in presence of hydrogen. The combustion of this gas is effected by mixing it with a considerable quantity of air and aspirating the mixture through a short tube containing cupric oxide heated to redness in a small combustion furnace, the carbon dioxide which is produced being absorbed in standard baryta solution, which is afterwards titrated with standard oxalic acid.

Drehschmidt finds (Ber. 1888, 21, 3249) that a mixture of methane and oxygen can readily be burnt in a platinum tube, as above, if the latter is heated to bright redness. The contraction is observed, and the carbon dioxide formed is removed and the volume again measured.

Nitric oxide is converted into peroxide by admixture with oxygen, and the peroxide is absorbed by caustic potash, the excess of oxygen being afterwards absorbed by alkaline pyrogallate. Nitric oxide may also be absorbed by a concentrated solution of ferrous sulphate, but this method does not give such satisfactory results.

Nitrogen peroxide and nitrous anhydride, by titration; by absorption with sulphuric acid of sp.gr. 1·84; or, in absence of carbon dioxide and other absorbable gases, by absorption with caustic potash.

Olefines, by absorption with fuming sulphuric acid, acid vapours being removed by caustic potash; or by absorption in bromine water, bromine vapours being afterwards removed by caustic potash.

Oxygen, by absorption with alkaline pyrogallate. If the oxygen is present in greater proportion than 20 p.c. a small quantity of carbon monoxide is evolved from the pyrogallol during absorption, and hence the results are slightly too low. After treatment with pyrogallol the gas may be passed into the cuprous chloride bulbs in order to remove any carbon monoxide that may have been formed. Usually, however, this error has no material influence on the results. Oxygen may also be absorbed by phosphorus, and this has the advantage that the presence of carbon dioxide is without influence on the result. The temperature, however, must not be below 18°, and the absorption is prevented by the presence of ammonia, olefines, and other hydrocarbons, alcohol, &c.

Sodium hydrosulphite has been recommended as an absorbent for oxygen, the reaction

$$Na_2S_2O_4+H_2O+O=2NaHSO_3$$

taking place readily at low or high temperatures. The solution contains 50 grams of the salt and 40 c.c. of sodium hydroxide (5 : 7) in 250 c.c. of water, and is used in a pipette filled with rolls of iron-wire gauze (Ber. 1906, 39, 2069).

Oxygen may also be estimated by combustion with hydrogen, either explosively by the spark or over palladium-asbestos. The hydrogen should be evolved from commercial 'pure' zinc and pure dilute sulphuric acid, or in special cases from magnesium and sulphuric acid. One-third of the contraction consequent upon combustion gives the volume of the oxygen.

Sulphur dioxide, by titration.

In the ordinary gases from flues, generators, &c., the constituents are estimated in the following order: Carbon dioxide, olefines and benzene, oxygen, carbon monoxide, hydrogen, methane, nitrogen (as residue or by difference).

If acid vapours are present together with one or more of the above gases, the order of absorption, &c., must be determined by circumstances.

Apparatus and manipulation.

Collecting samples.—The gas to be analysed is usually drawn from the flue, chamber, &c., by aspirating it through glass tubes, which may be termed conducting tubes. When the temperature is high, porcelain tubes may be used; or if the gas has no acid properties, iron tubes can be employed. When samples are constantly taken from the same flue, &c., it is convenient to have a short piece of porcelain or iron pipe cemented into the wall and closed at the outer end with a plug, which is readily removed when the sample is taken. In cases where the gases are originally at a high temperature and possibly in a state of partial dissociation, it is important to draw the sample slowly through a somewhat long tube in order that the gas may cool slowly, since rapid cooling of the gases may leave them in a partially dissociated condition and thus lead to erroneous results.

The sample may be conveniently collected in the measuring apparatus itself; but where this is not possible, a cylindrical glass tube A, drawn out at the upper end and connected with a stop-cock and capillary tube, and drawn out at the lower end and connected by caoutchouc tubing with a similar tube B, open at the top, makes a convenient sampler. The collecting tube may with advantage be provided with a stop-cock at the bottom. The vessel A is completely filled with water or mercury by raising B to a higher level, and the upper stop-cock is closed. The capillary tube is connected with the conducting tube, and the vessel B is lowered so that when the stop-cock is slowly opened the gas is drawn into A, and the water or mercury collects in B. When A is filled the stop-cocks are closed. The gas is readily transferred from A to the measuring vessel by raising B and carefully opening the stop-cock.

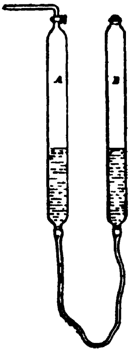


FIG. 35.

In all cases the air in the conducting tube must be expelled, and this is done by placing a T-tube between the end of the tube and the collecting vessel. This T-piece is connected with an aspirator, and the tube is filled with the gas before the stop-cock of the collecting vessel is opened. When the collecting vessel is provided with a three-way cock, the aspirator may be connected directly with the latter. Various forms of aspirator may be used. When the volume of gas to be aspirated is small (*e.g.* in removing air from the conducting tube), a small globular indiarubber aspirating pump is very convenient. For larger quantities of gas, glass bottles with a tubulus or stop-cock at the bottom and a tube or stop-cock at the top, or similar vessels of sheet zinc, may be used (Figs. 36 and 37). They are filled with water, the upper tube being connected with the tube which passes into the flue, and the water is allowed to flow from the tap at the bottom. The volume of gas aspirated is determined by measuring the volume of water which flows from the aspirator, and correcting this volume for temperature, &c., in the usual way (*v.* ASPIRATOR).

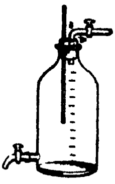


FIG. 36.

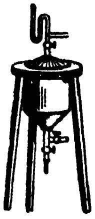


FIG 37.

When aspiration is to be continued for a long time, one of the various forms of water pump may be used. The volume of air aspirated in a given time with a given pressure of water may be determined once for all by direct measurement, or a small gas meter may be placed between the pump and the vessel into which the gas is passed.

If the gas has to be kept for some time before analysis, or if it has to be transported from one place to another, it may be collected in glass tubes which have previously been drawn out at each end. As soon as the tubes are full, the ends are closed by stoppers of indiarubber tubing and glass rod, or are hermetically sealed by fusion. If the quantity of gas is large, cylindrical zinc vessels with conical ends closed by indiarubber corks answer very well.

(For other forms of gas-samplers, *v.* J. Soc. Chem. Ind. 1889, 8, 176; 1903, 22, 190.)

Estimations by titration.—A measured quantity of the appropriate standard solution is placed in a flask or a Woulff's bottle fitted with two tubes, one of which dips into the liquid and is connected with the tube placed in the flue, &c., whilst the other ends just below the cork and is connected with an aspirator. After aspiration has been continued for a sufficient length of time, the excess of reagent is determined by titration. The volume of gas aspirated is determined by the volume of water which has run from the aspirator or by means of a gauge attached to the aspirator. This volume of water, however, represents a volume of gas saturated with moisture and at a temperature and pressure which must be determined by means of a thermometer attached to the aspirator and a barometer in close proximity; the volume under standard conditions is calculated in the usual way. In calculating the percentage composition of the gas, it must be borne in mind that the original volume of the gas was the sum of the volumes of the absorbed constituent and the volume which has passed into the aspirator.

If V_1 is the volume of the absorbed gas, and V_2 the volume which has passed into the aspirator, both under standard conditions, then

$$\frac{100 \times V_1}{V_1 + V_2} = \text{per cent. of } V_1 \text{ by volume.}$$

This method may be applied in the estimation of—

Ammonia, by absorption in sulphuric acid and titration with alkali.

Carbon dioxide (in small quantities), by absorption in standard baryta solution and titration with oxalic acid.

Chlorine, by absorption in a standard solution of arsenious oxide in sodium carbonate, and subsequent titration with iodine after saturating with carbon dioxide.

When hydrochloric acid and chlorine occur together, the latter is determined separately in one quantity, and a second quantity is absorbed in the solution of arsenious oxide in sodium carbonate free from chlorine, and the total chlorine is determined by titration with silver nitrate, using Volhard's thiocyanate method. In calculating the percentage composition, it is important to remember that 1 vol. of chlorine produces 2 vols. of hydrochloric acid.

Hydrochloric acid, by absorption in sodium carbonate and titration with silver nitrate, or, in absence of carbon dioxide and other acids, by absorption in standard caustic potash or soda, and subsequent titration with an acid.

Hydrogen sulphide, by absorption in standard iodine and titration with thiosulphate; or by absorption in bromine water and gravimetric estimation as barium sulphate.

Nitrogen oxides, by absorption in acidified permanganate solution of definite strength, the gas being passed until the solution is just decolourised. This method gives the amount of nitrogen oxides in terms of their reducing power.

Sulphur dioxide, by absorption in standard iodine solution and titration with thiosulphate, or by absorption in bromine water and gravimetric estimation as barium sulphate. The latter plan may be adopted when the proportion of sulphur dioxide is very small and a large volume of gas must be aspirated.

Measuring and absorption apparatus.—Only those forms which have come into general use and are of wide applicability will be described here. Descriptions of the numerous other modifications will be found in Winkler's Chem. Unters. der Industrie-Gase; Winkler and Lunge's Technical Gas Analysis; and in Zeitsch. anal. Chem.

An extremely convenient device which is applied to almost all the forms of apparatus is the three-way stop-cock. This has the usual transverse bore, but the plug itself is elongated in the form of a tube, the bore of which is continued in a curved direction through the plug and opens at the side in the same plane, but in a direction at right angles to the transverse bore. By means of this tap two tubes can be made to communicate with one another, or either of them separately can be put in communication with a third tube or with the air.

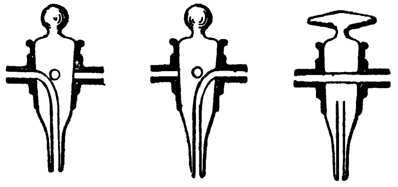


Fig. 38.

Orsat's apparatus.—The measuring tube or burette consists of a cylindrical bulb terminating at one end in a capillary tube and at the other in a narrow tube of uniform bore graduated in tenths of a cubic centimetre. The total capacity of the tube from the zero to the capillary is 100 c.c., and the lower end of the tube is connected by caoutchouc tubing with a 'level-bottle,' the height of which can readily be adjusted. The burette is enclosed in a cylinder which is filled with water at a constant temperature. The capillary from the upper end of the measuring tube is carried horizontally along a wooden support. Other capillary tubes provided with stop-cocks are fused into it at right angles and communicate by means of very short lengths of stout indiarubber tubing with the absorption pipettes, each of which consists of a pair of somewhat large cylindrical bulbs communicating at the bottom by a curved tube. The bulbs nearest the capillary tubes are fitted with short lengths of glass tubing so that a large surface of the reagent may be exposed, and the other bulbs receive the liquids when they are driven out from the first bulbs by the gas. Any number of bulbs can, of course, be attached to the main capillary, and at the end of it there is a three-way tap communicating with the aspirating tube or with the air.

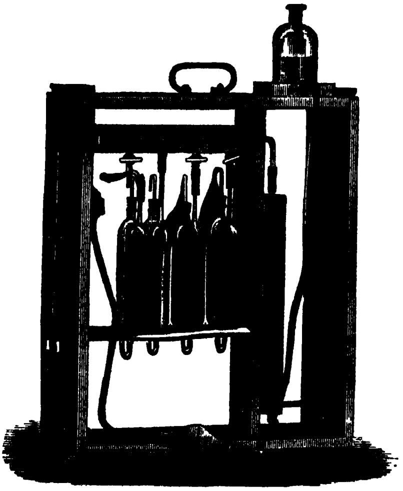


Fig. 39.

The three absorption pipettes indicated in Fig. 39 are generally filled respectively with solutions of caustic potash, alkaline pyrogallate, and cuprous chloride, and serve for the estimation of carbon dioxide, oxygen, and carbon monoxide.

The burette is filled with water by placing the liquid in the level-bottle and raising the latter, and the stopcocks are then closed. The absorption bulbs are rather more than half filled with the liquid reagents, and by opening the stop-cocks and placing the level-bottle below the apparatus the liquids are drawn up so as to fill completely the bulbs connected with the capillaries. The stop-cocks are then closed.

The burette is filled with water up to the capillary tube by raising the level-bottle, and the far end of the capillary tube is connected with the tube along which the gas is to be conducted. The lower end of the three-way tap is connected with an indiarubber aspirator, and the air is removed from the conducting tube by aspirating the gas through it. The level-bottle is then lowered, the tap is turned through 90°, and the gas is drawn into the burette. When a sufficient volume has entered, the tap is closed, the levels inside and outside the burette are adjusted by raising the level-bottle, and the volume of the gas is read off as soon as the temperature is constant. If it is desired to operate upon exactly 100 c.c., the gas is drawn in until the water is a little below the zero, the tap is closed and the level-bottle is raised so that the gas is slightly compressed and the water rises above the zero (time having been given for the liquid to run down from the sides of the burette), and the indiarubber tube is closed by a pinch-cock. The level-bottle is again lowered, and by cautiously opening the pinch-cock the water is allowed to descend exactly to the zero, and the pinch-cock is closed. The tap at the end of the main capillary is opened for an instant, so that the excess of gas may escape and the 100 c.c. remaining in the burette may be at atmospheric pressure.

In order to bring the gas into any one of the absorption bulbs, the level-bottle is raised and the tap of the particular bulb is opened. The gas passes into the bulb, and by alternately raising and lowering the level-bottle the gas can be passed backwards and forwards several times, care being taken that the absorbing liquid does not pass through the stop-cock. The gas is finally drawn off so that the absorbing liquid just reaches the stop-cock, the latter is closed, and, after readjusting the levels, the volume of gas is again read off. After making the necessary corrections, the decrease in volume is, of course, the volume of the gas which has been absorbed. The order in which the absorbing liquids should be applied has already been given (p. 236).

Lunge has added to this apparatus a capillary tube with palladium asbestos, for the estimation of hydrogen, connected with a bulb similar to the absorption bulbs, but containing water only. The apparatus also contains a small spirit-lamp carried by a movable rod for heating the palladium asbestos (Dingl. poly. J. 1882, 245, 512).

Sodeau has introduced a modification of Orsat's apparatus suitable for the analysis of mixtures containing only small proportions of combustible gases (*e.g.* chimney gases). In this modification the cuprous chloride pipette and the palladium combustion tube are replaced by a combustion pipette, the only absorption pipettes present being those containing caustic potash and alkaline pyrogallate. The carbon dioxide is first estimated by means of the former, and the combustible gases burnt by passing an electric current (5 amperes) for a short time through a platinum spiral in the combustion pipette. The contraction is noted, and the carbon dioxide produced is estimated by absorption in the caustic potash. These data give the proportions of carbon monoxide and hydrogen originally present in the gaseous mixture. The residual oxygen may now be estimated by absorption in the alkaline pyrogallate (Chem. News, 1904, 89, 61).

Bone and Wheeler's apparatus is a simple form of gas apparatus capable of giving accurate results with almost all gaseous mixtures ordinarily met with in technical practice. The working liquid is mercury, and the apparatus consists of the following parts: (1) A water-jacketed combination of measuring and pressure tubes, A and B, communicating through the glass tap C with the mercury reservoir D; (2) an absorption vessel, F, standing over mercury in a mahogany trough; (3) an explosion tube, E, fitted with firing wires, and having a separate mercury reservoir, H; (4) a sampling tube, K. The connections between A, E, and F are of capillary bore throughout, with suitable glass taps. Before an analysis the whole of the apparatus, including the connections, is filled with mercury, and the gas may be introduced either from the sampling tube, K, or from the absorption vessel, F.

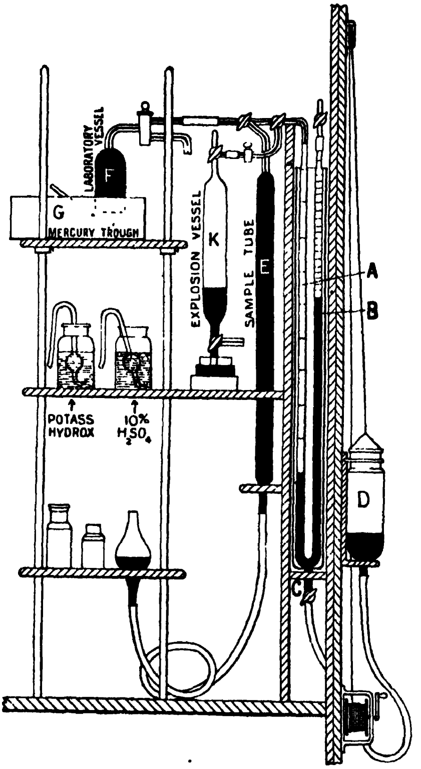


FIG. 40.

The Regnault-Frankland principle of measurement is employed, namely, the measurement of the pressure of the gas (in mm. of mercury) at constant volume. The measuring tube A has a series of constant-volume marks coinciding with the 0, 100, 200, &c., mm. marks on the pressure tube B. These two tubes are moistened with dilute sulphuric acid (1 : 20) as a precaution against the accidental introduction of alkali into the measuring tube. The tap closing the upper end of the pressure tube is connected to it by stout indiarubber pressure tubing; this gives a tight but elastic joint, and obviates risks of fracture. By means of this tap the pressure tube can be rendered vacuous, and, in this way, the measurements are rendered independent of the barometric pressure, and it becomes possible to analyse smaller volumes of gas. The length of the pressure tube provides for the requisite dilution of the explosive mixtures in analyses by explosion. All the absorptions are carried out in the same vessel, F, a comparatively small amount of freshly prepared reagent being used in each operation. The absorption vessel is rinsed out by means of the three-way tap, the lower parallel limb of which is joined to a large bottle connected up with the water pump. In this way a series of absorptions can be carried out without disturbing a single connection in the apparatus. An analysis of producer gas is easily completed in 45 minutes, and one of coal gas requires about an hour (J. Soc. Chem. Ind. 1908, 27, 10). (For other forms of technical gas apparatus, *v.* F. Fischer, Zeitsch. angew. Chem. 1890, 3, 591; Sodeau, J. Soc. Chem. Ind. 1903, 22, 187. *See* also Chem. Soc. Trans. 1894, 65, 43; 1899, 75, 82; Ber. 1902, 35, 3485, 3493; 1907, 40, 4956; J. Soc. Chem. Ind. 1908, 27, 483, 491; Chem. Zeit. 1903, 845; 1904, 086; Zeitsch. angew. Chem. 1907, 20, 22.)

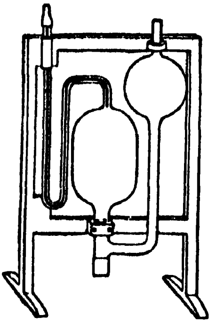


FIG. 41.

Hempel's apparatus.—The measuring apparatus consists of a burette, and a plain tube of the same length and diameter, which serves as a level-tube. The burette holds 100 c.c. from the zero to the capillary, is graduated in fifths of a c.c., and terminates at the top in a capillary tube to which is fitted a short piece of stout-walled caoutchouc tubing closed by a pinch-cock. Both the burette and the level-tube are fixed at the bottom into heavy circular stands, and each has a side tubulus near the bottom over which is slipped the caoutchouc tube by which they are connected. It is advisable to make all the joints secure with copper wire. In order to make the measurements more accurate, the burette may be surrounded by a wider tube filled with cold water (Winkler).

The pinch-cock is opened and both tubes are rather more than half filled with water. The burette is completely filled with water by raising the level-tube until the water runs out of the indiarubber tube at the top, and the pinch-cock is then closed. By means of the indiarubber tube the burette is attached to the conducting tube, which has already been filled with the gas, the level-tube is lowered, and the pinch-cock opened. When sufficient gas has been drawn in the pinch-cock is closed, the levels adjusted, and the volume read off in the usual manner. If it is desired to admit exactly 100 c.c., proceed in the same way as described under Orsat's apparatus.

The reagents are contained in absorption pipettes. Simple absorption pipettes consist of two bulbs which communicate at the bottom by a bent tube, one bulb being at a higher level than the other (Fig. 34). The upper part of the lower bulb terminates in a straight capillary tube, which extends to a slightly greater height than the higher bulb, and serves to connect the pipette with the burette. In the tubulated pipette the bottom of the lower bulb is provided with a tubulus, which can be closed with a caoutchouc stopper, and through which solid reagents such as phosphorus or zinc can be introduced. A composite absorption pipette consists of two similar pairs of bulbs, the second pair containing water or some other liquid which protects the reagent in the first from the action of the air. Composite pipettes are used with alkaline pyrogallate, cuprous chloride solution, bromine water, and similar reagents (Fig. 42)

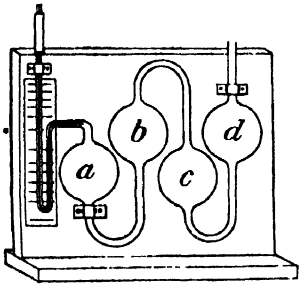


FIG. 42.

Cumming (J. Soc Chem. Ind. 1913, 32, 9) has modified the Hempel double pipette by the addition of a side tube to the top of *b*, which can be closed by a rubber cork. The reagent is poured through the side-tube on *b*, and water is poured in through *d* to form a water-seal.

In making the absorptions the pipettes, which are attached to wooden stands, are placed on a table stand of such height that the top of the capillary of the pipette is level with the top of the capillary of the burette. The burette and pipette are joined by means of short pieces of caoutchouc tubing and a short piece of capillary tube bent twice at right angles. The volume of air contained in this capillary is so small that it does not introduce any appreciable error. Care is taken that the capillary of the absorption pipette is filled just up to the top with the reagent. The connections being made, the level-tube, which should be full of water, is placed on the table stand and the pinch-cock is opened. The gas passes into the pipette, and by raising and lowering the level-tube the whole of the gas can be passed backwards and forwards two or three times; or the gas may be allowed to remain in contact with the liquid in the pipette. When absorption is complete, the level-tube is lowered until the reagent is drawn just up to the top of the capillary of the pipette, the pinch-cock is closed, and a second reading is taken.

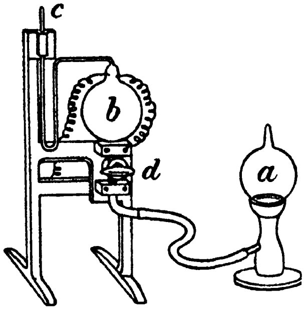


FIG. 43.

When combustions of hydrogen or carbon monoxide have to be made, the capillary tube containing palladium asbestos is inserted between the burette and a simple absorption pipette containing water only. With gases containing both methane and hydrogen, the combustion is conveniently effected in an explosion pipette of spherical form, in which mercury is used as the working liquid. The two bulbs of the pipette are connected by thick-walled indiarubber tubing, and the explosion bulb can be closed by two stop-cocks.

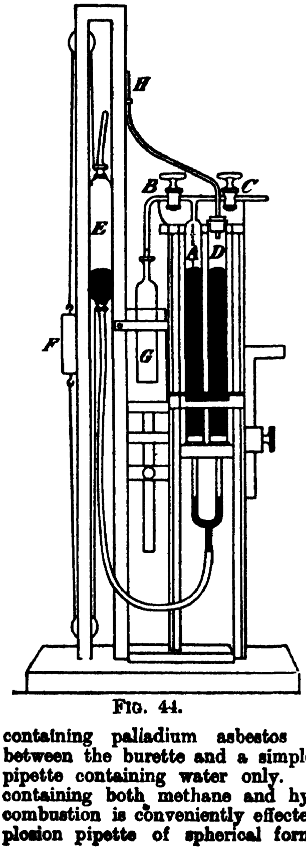


FIG. 44.

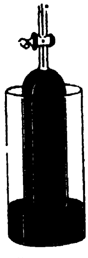


FIG. 45.

When gases very soluble in water have to be measured, a burette is used, provided at the top with a three-way stop-cock, the volume between them being exactly 100 c.c. The burette must be perfectly dry before being filled, an end which is most quickly effected by rinsing the burette with water, then with alcohol, and finally with ether, and passing a current of warm air through it. The lower end of the burette is connected with the conducting tube by means of the three-way tap *d*, the other end is connected with an aspirator, and a current of the gas is drawn through the burette until the air is completely expelled. The stop-cocks are then closed, care being taken that the gas in the tube is at atmospheric pressure. The absorptions, &c., are made in the same way as with the ordinary burette.

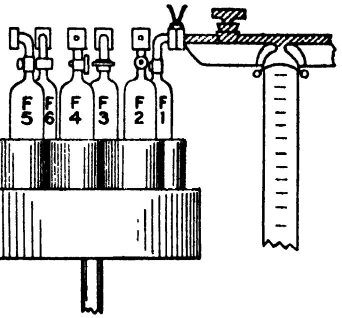


FIG. 46.

Stead's apparatus consists (Fig. 44) of a graduated tube A, in which all measurements are made, fitted with taps B and C, leading respectively to the absorption vessel and the sampling tube. The lower end of A is joined by means of a T-piece to the mercury reservoir E, and to the tube D, which is open to the atmosphere at H. The readings are taken under atmospheric pressure. The gas sample is collected either directly in the laboratory vessel G or in Stead's sampling apparatus (Fig. 45). From either of these reservoirs a portion of the gas is introduced into the apparatus at C, and thence by opening B into the laboratory vessel G, which contains caustic potash solution standing over mercury. If the gas consists practically of carbon dioxide, carbon monoxide, and hydrogen, it is then mixed with a known volume of oxygen,

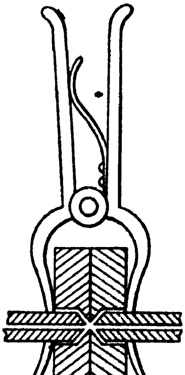


FIG. 47.

and the mixture sparked by means of platinum terminals fused into the upper part of the graduated tube A.

The contraction is ascertained and the carbon dioxide produced is estimated, and from these data the amounts of carbon monoxide and hydrogen are determined.

When other absorbable gases are present, then six absorption vessels are employed, and these are carried on a turn-table, so that each in turn can be brought into contact with the measuring tube (Fig. 46). In this modified form of the apparatus the eudiometer tube and each of the absorption vessels are fitted with a perfectly flat piece of plate glass perforated in the centre. These plates are lightly smeared with oil, and when communication is to be made between the eudiometer and the absorption vessel, these face plates are held together by a spring clip (Fig. 47).

A further improvement consists in the use of the modified form of absorption vessel shown in Fig. 48, in which the reagent is contained in a glass bottle closed by an indiarubber bung carrying a small glass stopper and a pipette furnished with a tap.

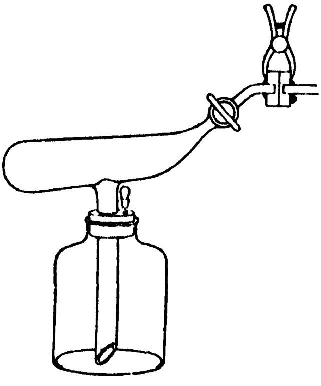


Fig. 48.

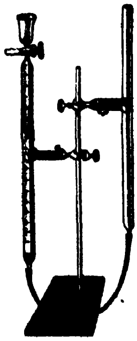


Fig. 49.

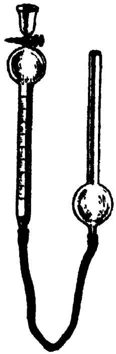


Fig. 50.

By means of these additions Stead's apparatus can be used for the complete analysis of furnace and producer gases and other technically important gaseous mixtures (J. Soc. Chem. Ind. 1889, 8, 178).

The nitrometer, originally devised by Lunge (Ber. 1878, 11, 436) for the estimation of nitrogen oxides in oil of vitriol, is capable of being applied to gas analysis and a large number of other determinations. It consists (Fig. 49) of a burette, fitted at the top with a three-way tap and a cup-shaped funnel, and communicating at the bottom by means of caoutchouc tubing with a plain tube of the same diameter, which serves as a level-tube. When large quantities of gas have to be measured, the upper part of the burette is expanded into a bulb, and there is a similar bulb on the level-tube (Fig. 50).

This apparatus is used with mercury, and is thus suitable for the analysis of gases soluble in water. It can be used in the same way as Hempel's burette, and for all purposes to which the latter is applicable. It may also be used without absorption pipettes, the reagent being introduced by means of the cup, but since the reagents cannot be removed without removing the gas, the latter method is only applicable when the reagents do not interfere with each other—*e.g.* for the absorption of carbon dioxide by caustic potash, followed by the absorption of oxygen by alkaline pyrogallate.

The estimation of nitrogen oxides in solution in sulphuric acid is conducted in the following manner. The apparatus is filled with mercury, so that when the tap is open between the burette and the cup, and the level-tube is raised, the mercury just passes through the tap and stands at a height of about 2 inches in the level-tube. The tap is then closed and 2–5 c.c. of the sulphuric acid, according to the quantity of nitrogen oxides which it contains, is placed in the cup, the level-tube is lowered and the tap is turned so that the acid is nearly all drawn into the burette without any air being admitted. To avoid measuring out small quantities (0·5–1 c.c.) of highly nitrated acid, this liquid should be diluted with a known volume of pure concentrated sulphuric acid, and 5 c.c. of this solution taken for analysis. The cup is rinsed with two successive quantities of 2–3 c.c. of pure acid, which is drawn into the cup with the same precaution as before. The tap being closed, the burette is taken out of the clamp and agitated in such a manner that the liquid is brought thoroughly into contact with the first 10 cm. or so of the mercury, which is broken up into bubbles. Nitric oxide is formed and collects in the upper part of the tube. When no more gas is given off, the levels are adjusted and the volume read off after the froth has subsided. In adjusting the levels the difference between the specific gravity of the acid and the mercury is allowed for by taking 6·5 mm. of acid = 1 mm. of mercury. A small quantity of acid is placed in the cup and the tap opened: if the acid is drawn in the pressure in the burette was too low; if gas escapes, the pressure was too high. It is better to err on the side of too low pressure, which is readily corrected by allowing acid to run in from the cup and taking another reading.

In agitating, care should be taken that the drop of acid which collects in the top of the burette just below the tap does not escape contact with the mercury, otherwise the results will be too low.

To prepare for another estimation, the level-tube is raised and the tap is opened so that all the acid and some of the mercury is driven into the cup, and the tap is then turned so that the acid runs out at the side.

The nitrometer may be used for the valuation of nitrites and nitrates, which are introduced in the form of a concentrated aqueous solution, care being taken that the proportion of water to acid does not exceed 2 parts of aqueous solution to 3 parts of the strongest acid. It may also be used for the estimation of nitrates and nitrites in potable waters, and in fact for almost any determinations in which a definite volume of gas is given off. For example, the estimation of carbonic acid; of urea by hypobromite (the reading being increased by 9 p.c. to correct for solubility of the gas and incomplete decomposition); hydrogen peroxide by an acidified solution of potassium permanganate, or, *vice versa*, the value of a permanganate solution by means of hydrogen peroxide, &c. (*See* Lunge, Ber. 1878, 11, 436; J. Soc. Chem. Ind. 1885, 4, 447, and 1886, 5, 82; Zeitsch. anal. Chem. 25, 309; and the translation of Winkler's Technical Gas Analysis (1885); also Allen, J. Soc. Chem. Ind. 1885, 4, 178.)

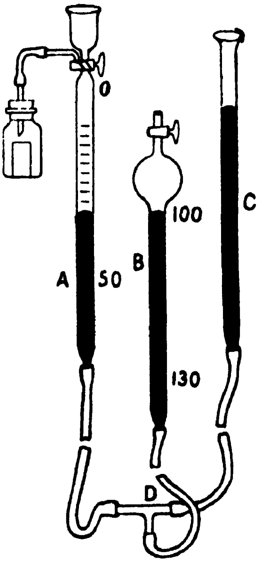


Fig. 51.

The *gas-volumeter*. Several of the estimations referred to in the preceding paragraph are more conveniently carried out in the gas-volumeter devised by Lunge, as in this apparatus the decomposition can be effected in a separate vessel. The measuring tube A and the reservoir C are converted by means of the T-piece D, with the so-called 'reduction' tube B.

At the outset the temperature and pressure are observed, and the volume occupied under these conditions by 100 c.c. of dry (or moist) air measured at 0° and 760 mm. is calculated. The reduction tube is filled with air to this volume, and the tap of the tube closed, or the end of the reduction tube may be terminated by a capillary and sealed off after the volume has been correctly adjusted. A special tap for the reduction tube has been devised by Göckel (Zeitsch. angew. Chem. 1900, 13, 961, 1238). If moist gases are to be measured, a small drop of water is introduced into the reduction tube; if dry gases are under examination, a drop of concentrated sulphuric acid must be introduced into the reduction tube. The formulæ for calculating the volume of gas in the reduction tube are as follows :—

$$V_1 \text{ (dry gases)} = \frac{V_0(273+t)760}{273 \times B}$$

$$V_1 \text{ (moist gases)} = \frac{V_0(273+t)760}{273(B-f)}$$

where V_1 = volume of gas required;
V_0 = normal volume (*e.g.* 100 c.c.);
t = observed temperature;
B = observed barometric pressure;
f = tension of water vapour at observed temperature.

When a decomposition by sodium hypobromite or hydrogen peroxide has been carried out in the auxiliary generating bottle, the gas evolved passes into the measuring tube A. The mercury in A and C are then adjusted to the same level, and the tap *o* closed, the gas being then at the atmosphere pressure. The three tubes are now adjusted so that the mercury in A and B are at the same level when the mercury in the latter tube stands at the 100 c.c. graduation. The gases in A and B are at the same temperature and under the same pressure, and since the gas in B occupies the same volume as it would at 0° and 760 mm. pressure, it follows that the gas in A also occupies the same volume as it would under the standard conditions. In this way, by the use of the gas-volumeter, all thermometric and barometric readings and all reductions by calculations or special tables are avoided; for the volume of gas is read off directly under conditions corresponding to the normal pressure and temperature. It is, however, essential that the reduction tube should be arranged for dry or moist gases according to the nature of the analytical operation involved (*v.* Lunge, Ber. 1890, 23, 440; 1891, 24, 729; 1892, 25, 3157; Zeitsch. angew. Chem. 1890, 3, 129; 1891, 4, 197, 410; 1892, 5, 677; J. Soc. Chem. Ind. 1890, 9, 547. *Cf.* Gruskiewicz, Zeitsch. anal. Chem. 1904, 43, 85).

In addition to the hypobromite and hydrogen peroxide decompositions, Lunge and Marchlewski have adapted the gas-volumeter to the estimation of carbon dioxide in natural carbonates, Portland cement, and other mineral substances, and also to the determination of carbon in iron and steel (Zeitsch. angew. Chem. 1891, 4, 229; 1893, 6, 395; J. Soc. Chem. Ind. 1891, 10, 658). G. T. M.

Electrochemical Analysis.

The first suggestion to apply the electric current to the deposition of metals was made by Cruickshank in 1801 (Nicholson's Journal of Nat. Phil. 1801, 4, 254). He noticed that metals were deposited from acid or alkaline solutions of their salts at the negative pole, and that the metal went into solution at the positive pole. He therefore suggested that the electric current might thus be used as an aid to analysis, particularly for depositing lead, copper, and silver.

In 1812 Fischer suggested its use for detecting small quantities of arsenic (Gilbert's Annalen, 42, 92). In 1840 Cozzi (Arch. delle Scienze med. fis 50, ii. 208) employed the galvanic current (produced by plates of gold and zinc connected together by a wire) to ascertain whether organic fluids, such as milk, contained metallic impurities. Gaultier de Claubry (J.

Pharm Chim. iii. 17, 125) applied it to detect small quantities of arsenic in animal fluids. In 1861, Bloxam (Quart. Journ. Chem. Soc. 13, 12, 338) described an electrolytic method for detecting arsenic and antimony. Becquerel (Ann. Chim. Phys. 1830, 43, 380) found that manganese and lead were readily oxidised, and appeared as oxides on the anode.

All these workers appear to have merely used the electric current as an aid to qualitative analysis. Wolcott Gibbs (Zeitsch. Anal. Chem. 3, 334), in 1864, showed that copper, nickel, zinc, lead, and manganese might be quantitatively determined by means of the electric current. Lucknow (Dingl. Poly. J. 1865, 177, 231, and 178, 42), from 1860, had employed electrolytic methods for the quantitative analysis of copper salts and for commercial copper. From this time forward many workers entered the field, and about 1880 Edgar Smith in America, and Classen in Germany, very much advanced the subject of electro-analysis, and to-day it is one of the most useful helps to the analytical chemist.

Before dealing with the methods of deposition and separation of the metals, it will be well to describe the apparatus used; but only the apparatus most generally employed will be dealt with.

Classen first suggested the employment of a platinum basin as cathode and a platinum disc as anode. A convenient stand for holding the basin, and a method of connecting with the source of current, are shown in Fig. 52. The basin should hold from 150 to 180 c.c. of solution. The inner surface of the basin should be roughened by the sand blast, as this causes better adherence of the deposit, especially in the case of peroxides such as lead and manganese. The base of the stand is of slate or marble, and the brass rod which conveys the — current is hollow; through this brass rod an insulated wire for carrying the + current passes, and is connected at the top of the rod by means of a piece of ebonite. The ring which supports the basin has three little platinum points at equal intervals on its circumference; on these the basin rests, thus ensuring good contact. The positive pole of the source of current is connected with the binding-screw fixed to the slate base, and the negative pole with the binding-screw marked —. In dealing with metals which deposit as oxides on the positive pole the basin is connected with the + pole.

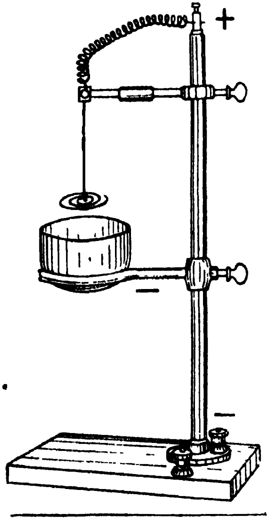


Fig. 52.

Another useful form of electrode is illustrated in Fig. 53. The anode is a stout spiral of platinum and the cathode is a cylinder of platinum gauze. This form of electrode can be employed either for stationary work or for rapid deposition work when the anode is rotated. The vessel in which the electrolysis takes place may either be a beaker or, better, a funnel with a tap such as is illustrated in Fig. 67.

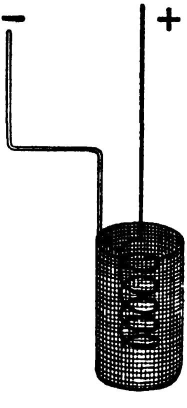


Fig. 53.

For stationary work the Flag electrode of F. Mollwo Perkin (Fig. 54) gives very satisfactory results. The cathode consists of a small sheet of stout platinum gauze, autogenously fastened on to a rigid platinum-iridium frame, both frame and gauze being roughened by the sand blast. The wire holds the electrode in position during the analysis. The loop near the top of the wire serves to hang the electrode on the balance. The anode is made of platinum wire, and is bent upon itself in such a way that when it is placed in position for electrolysis, as illustrated in Fig. 55, an even density is obtained on all parts of the cathode.

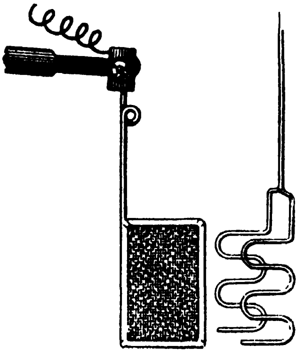


Fig. 54.

It has been found that the rate of deposition of metals from their solutions is very much increased and higher current densities can be employed when either the anode or cathode is rapidly rotated. Frary (Zeit. f. Elektrochem. 1907, 308) has also shown that excellent results can be obtained by electrolysing with stationary electrodes, but causing agitation of the electrolyte by placing the whole apparatus in the field of a powerful electromagnet. The forms of the apparatus are depicted in Fig. 56. From the figure it is seen that the solution is contained in a beaker B, in which is a cylindrical platinum gauze cathode C and a heavy platinum wire as anode A. The beaker is placed in the centre of a spool made from insulated copper wire E. By passing an electric current through the copper wire of the spool, a powerful magnetic field is produced, in the centre of which the beaker stands. If now a current be passed through the electrolyte by means of the electrodes, the electric lines of force are cut at right angles by the magnetic lines of force, and this produces a tendency for the solution to rotate, owing to the vertical magnetic field and radial current lines. The speed of rotation depends upon the ratio between the electric current and the magnetic current. With an electrolysing current of from 6 to 7 amperes, Frary was able to deposit 0·850 gram copper in 15 minutes. The other form, illustrated in Fig. 57, is for electrolysing with a mercury cathode, the use and applications of which will be described later. The electrolysing vessel is ring-shaped, so that it may fit into a hole cut into the pole D of the magnet. An iron rod passes from the other pole up into the centre of the electrolysing vessel. A is the anode and C the cathode. Extremely rapid rotation is thus produced, because the iron core very much facilitates the passage of the magnetic current, there being a radial field with vertical current lines.

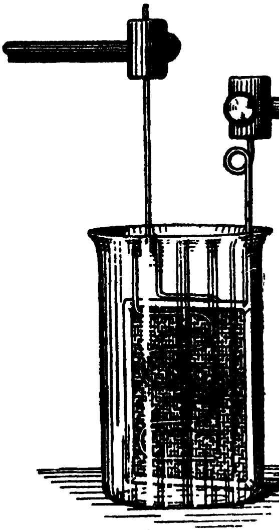


FIG. 55.

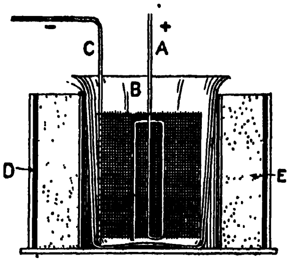


FIG. 56.

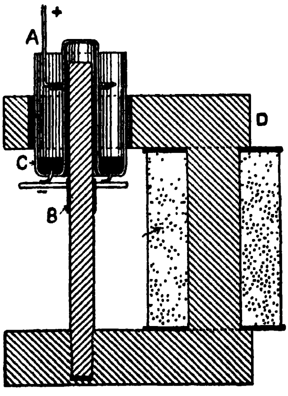


FIG. 57.

The advantages claimed for this method are: rapidity of deposition, and, as there are no mechanical parts which require lubrication, there is no chance of contamination from oil, or grease accidentally falling into the solution. As a matter of fact, however, rapid methods of electrolysis are more frequently carried out by means of a rotating anode or cathode.

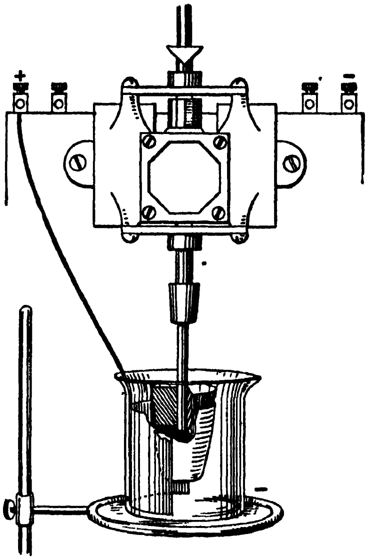


FIG. 58.

Gooch and Medway (Amer. J. Sci. 15, 320) use a rotating cathode. It is made from a platinum crucible of about 20 c.c. capacity. The crucible is attached to the shaft of the electromotor, which is used to rotate it at a speed of from 600 to 800 revolutions per minute by fitting it over a rubber stopper with a central bore, into which the end of the shaft fits tightly. In order to make electrical connection between the crucible and the shaft of the motor, a narrow strip of sheet platinum is soldered to the shaft and bent upwards along the sides of the stopper. This connects the shaft with the inside of the crucible when the latter is pressed over the stopper. The anode consists of a half cylinder of sheet platinum. Fig. 58 represents the arrangement of the apparatus when fitted together.

F. Mollwo Perkin and W. E. Hughes (Trans. Faraday Soc. 1910, 14) use an electrode of sheet platinum spun up so as to form a narrow thimble (Fig. 59), the upper end being open and having a stout iridio-platinum wire fused on to it by means of three short wire supports. This electrode is fixed into a small chuck and rapidly rotated by means of an electromotor, the speed of rotation usually being from 750 to 950 revolutions per minute. When in use, about two-thirds of the length of the thimble is dipped

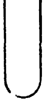


FIG. 59

into the electrolyte, the active surface being about 16·3 sq. cm. If dipped too deeply into the solution, there is a tendency for the liquid to splash into the interior of the cylinder, and this would, of course, lead to erroneous results. The anode consists of a platinum cylinder of fine mesh. It is, however, frequently more satisfactory to employ a rotating anode and a stationary cathode, and for this purpose the gauze anode is employed as cathode, and the anode consists of a spiral of stout iridio-platinum wire. The simplest arrangement is illustrated in Fig. 53. The electrolysing vessel consists of a tap funnel which, when the electrodes are covered, holds about 60 to 70 c.c. of solution. The advantage of this form of electrolysing vessel is the ease with which the electrolyte can be removed on the completion of the electrolysis and the electrodes washed. The method of procedure is to place a beaker beneath the tap and draw off the solution until about half of it has run in. Distilled water is then run up to the original mark and the solution drawn off as before. The operation is repeated until the ammeter needle sinks to zero. The remaining water is run off, the tap closed, and the funnel filled with pure methylated spirit. This is run off, and, after a final washing with absolute alcohol, carried out in the same manner, the electrodes are removed and the cathode dried in the steam oven.

Another form of rotating cathode devised by Perkin is illustrated in Fig. 60. The cathode consists of a cylinder of platinum gauze. The anode is in the form of a double circle of stout platinum wire, and has four small baffle plates so placed as to prevent it from rotating with the cathode.

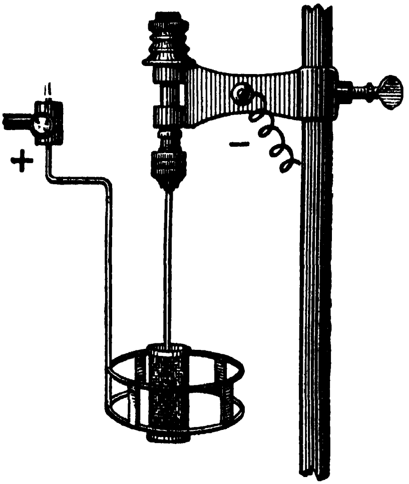


FIG. 60.

In order to rotate the anode (or cathode), it is fixed into a small chuck fastened on to the end of the spindle of a bicycle hub. The barrel of the hub has an arm fastened into it which can be clamped to any suitable support. The upper end of the spindle has a sheaf of pulleys fastened to it, so that it can be rotated by means of a belt from a motor and different speeds be obtained. It is found that the current passes very well through the barrel of the hub and the balls, which are lubricated with oil and graphite, to the spindle, and so to the electrode. When it is desired to obviate all drop in potential, *e.g.* if the apparatus is to be used for graded potentials, then a mercury cup is fastened on to the top of the spindle so that the current passes directly to the spindle.

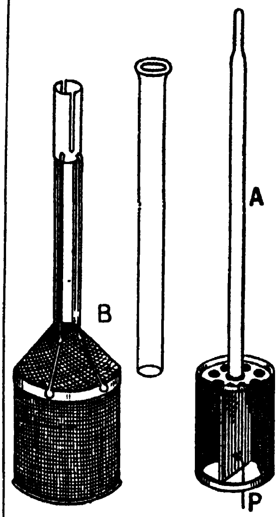


FIG. 61.

The apparatus of H. J. Sand (Trans. Chem. Soc. 1907, xvi. i. 373) is rather more complicated, but gives equally satisfactory results.

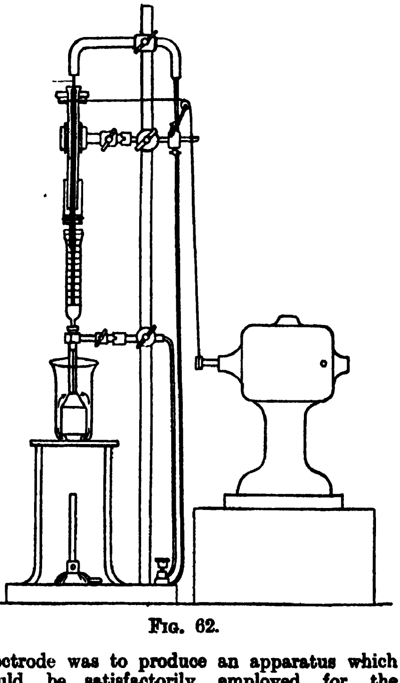


FIG. 62.

The special object in the design of this electrode was to produce an apparatus which could be satisfactorily employed for the separation of metals by graded potentials. It consists of a pair of platinum gauze electrodes (Fig. 61), an inner rotating electrode A, and an outer electrode B. The two are kept in position relatively to each other by means of a glass tube, which is slipped through the collar and the ring of the outer electrode B. It is gripped firmly by the former, but passes loosely through the latter. The hollow iridio-platinum stem A of the inner electrode is passed through the glass tube, in which it rotates freely. The mesh of the gauze is 14^2 per sq. cm. The gauze of the outer electrode almost completely stops the rotation of the liquid. The electrolyte is, therefore, ejected rapidly from the centre of the inner electrode by centrifugal force, and is continually replaced by liquid drawn in from the top and the bottom. So great is the suction thus produced, that when the electrode is moving rapidly, chips of wood or paper placed in the solution are drawn down to the top of the outer electrode. The circulation is practically independent of the size of the beaker employed. As the outer electrode surrounds the inner completely, the lines of flow of the current are contained between the two, and even when strong currents are employed, the potential of the electrolyte anywhere outside the outer electrode is practically the same as that of the layer of liquid in immediate contact with it. Fig. 62 shows the apparatus with stand and motor in working order. Before the method adopted for electrolysing by means of graded potential is discussed, the mercury cathode devised by Smith and Howard will be described.

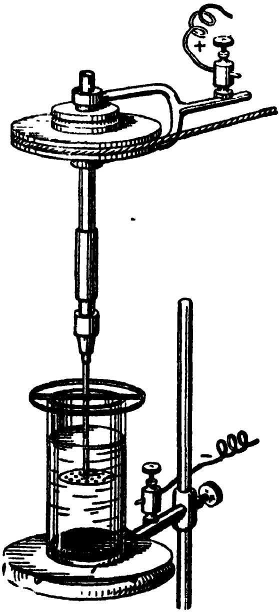


FIG. 63.

WolcottGibbs, in 1880, first suggested the use of metallic mercury as cathode, a definite amount being weighed into a beaker, where it was connected by means of platinum wire with the negative pole of a battery. Various metallic salt solutions were experimented upon, and, in 1883 (Amer. Chem. J. 13, 571), Gibbs stated that 'It was found possible to separate iron, cobalt, nickel, zinc, cadmium, and copper so completely from solutions of the respective sulphates that no trace of metal could be detected in the respective liquids.' Gibbs had in view not only the determination of the metals, but also of the anion left in the solution by titration.

In 1886 Luckow (Chem. Zeit. 9, 338, and Zeitsch. anal. Chem. 25, 113) suggested the addition of a known weight of a solution of a mercury salt to a solution of zinc sulphate, and so to deposit zinc and mercury simultaneously. In 1891 Vortman (Ber. 24, 2749) suggested a similar method, and employed it in the determination of several metals. Drown and McKenna (Amer. Chem. J. 5, 627) further worked at the subject, using an apparatus somewhat similar to Wolcott Gibbs, that is to say, an actual mercury cathode, but the process was first successfully worked out by Edgar Smith and his collaborators (J. Amer. Chem. Soc. 25, 885). The apparatus employed consists of a small tube or beaker of about 50 c.c. capacity, close to the bottom of which a thin platinum wire is introduced by means of which the current is supplied to the mercury cathode (Fig. 63).

The external part of the platinum wire touches a disc of sheet copper on which the beaker rests, and which is connected with the negative source of the current.

The anode is either a perforated disc of platinum or a stout spiral of platinum wire. During the electrolysis the anode is rapidly rotated by means of an electromotor or water turbine.

The chief difficulty in using the mercury cathode is the trouble experienced in washing and drying it. The solution left at the end of the electrolysis is siphoned off, and at the same time distilled water is run in until the needle of the ammeter drops to zero. Then, and not till then, the current is switched off. The inside of the beaker and the amalgam are rinsed with alcohol three times, and finally with dry ether. It is advantageous, in order to drive out thoroughly the last traces of ether, to blow dry air into the beaker for a few minutes. After standing for half an hour, the apparatus is ready for weighing. F. M. Perkin (Trans. Faraday Soc. 1910, 14) uses a small quartz beaker as containing vessel, with an iridium wire fused into it to make contact with the mercury. The advantage of iridium is that it does not amalgamate with the mercury. An advantage of the quartz vessel is that it can be heated to redness for purposes of cleansing. The apparatus is illustrated in Fig. 64. It will be noticed that a siphon tube is fused into one side of the beaker. The layer of mercury must not be sufficient in quantity to close the side tube. A spiral iridio-platinum anode is employed. When the electrolysis is finished, a piece of rubber tube is fastened to the bent end of the siphon. Distilled water is added so that the solution begins to siphon over into a beaker placed below the rubber tube. In order to work with as small a quantity of water as possible and in cases where the solution is required again, *e.g.*

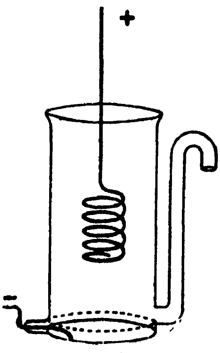


FIG. 64.

in metal separations, the solution is allowed to run out until its level drops almost to the end of the anode. Fresh water is then run in, and the operation repeated until the ammeter needle ponits to zero. For purposes of steadiness the vessel is held between clips on a copper plate.

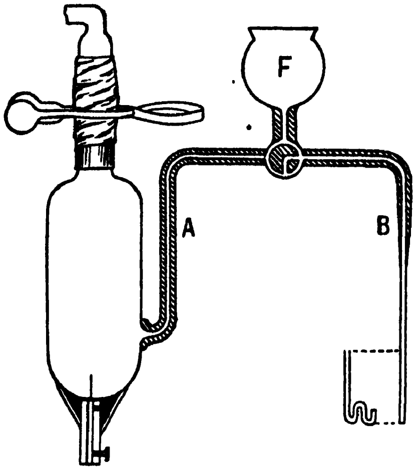


FIG. 65.

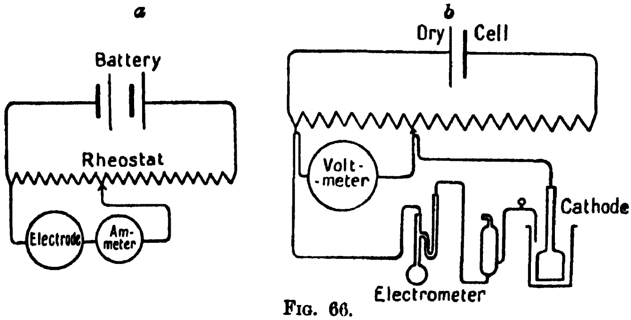


FIG. 66.

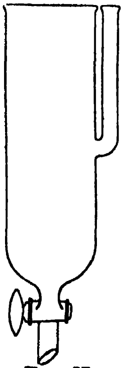


FIG. 67.

By means of the mercury cathode not only can the cations be rapidly and accurately determined, but also the anions remaining in the solution.

Various substitutes for platinum electrodes in electro-analysis have been suggested (*see* Nicolardot and Boudet, Bull. Soc. chim. 1918, [iv.] 23, 387), *e.g.* gold, gold-platinum alloys, copper, and certain proprietary iron-alloys. An alloy of gold (7) and platinum (1) serves well in all circumstances for cathodes. As anodes such electrodes are less satisfactory and must not be used for the anodic deposition of lead, nor with cyanide electrolytes, unless electro-plated with platinum. In ammoniacal solution such electrodes acquire a light brown colour, and increase slightly in weight, but return to their original weight and appearance when heated to 300° (Analyst, 1919, 38).

Method of Graded Potential.

Each metal has a particular potential at which it begins to be deposited; below this potential it is not possible to deposit the metal. It follows, therefore, that when dealing with a solution containing the salts of two or more metals it will be possible, provided the deposition potentials of the metals do not lie too near together, to deposit the metals separately, by first working with the lowest potential at which one of the metals will be deposited. When this metal has been deposited the next one in the potential series will be deposited by raising the potential.

This method of analysis was suggested by Kiliani in 1883, and was further elaborated by Freudenberg working in Ostwald's laboratory (Zeit. physikal. Chem. 12, 97). But it was H. J. S. Sand (Trans. Chem. Soc. 1907, 373) who first worked out the method and used the apparatus with the rotating cathode already mentioned. The potential is kept at constant value by means of an *auxiliary electrode.* Such an auxiliary electrode, designed by Sand, is illustrated in Fig. 65. It is a mercury-mercurous sulphate $2N$-sulphuric acid electrode. The distinctive feature of the electrode is in the funnel F, and connecting glass tube AB. The two-way tap allows the funnel F to be connected with either limb of the glass tube AB, or closes all parts from each other. The limb A permanently contains the $2N$-sulphuric acid solution of the electrode. But the limb B is filled for each experiment from the funnel F with a suitable connecting liquid, generally sodium sulphate solution. The end of B is made of thin tube of about 1½ mm. bore, and is bent round several times to minimise convection. While the electrode is in use, the tap, which must be kept free from grease, is closed, the film of liquid held round the barrel by capillary attraction, making the electrical connection, but towards the end of a determination, a few drops are run out in order to expel any salt which may have diffused into the tube.

Electrical connections.—For separations by graded potential the electrical connections must be made as shown in Fig. 66 *a* and *b*. The battery is connected directly to the two ends of a sliding rheostat, the electrolytic cell to one of them and the slider. It is essential that the sliding contact should be good. The arrangement adopted for the measurement of the potential-difference auxiliary electrode-cathode is one which has been frequently employed in electro-chemical research. The electromotive force to be measured is balanced against a known electromotive force by means of a capillary electrometer. The known electromotive force is drawn from a sliding rheostat, the ends of which are connected with one or two dry cells. The value of the E.M.F. is read directly on a delicate voltmeter (range 1·5 volts). For potential differences greater than 1·5 volts, a Helmholtz 1-volt instrument may be interposed between the auxiliary electrode and the rheostat. The arrangement allows the voltage to be measured almost instantaneously, which is a matter of great importance.

To carry out an experiment, the cathode, anode, and auxiliary electrode are placed in position, the electrolyte is heated to the required temperature, and covered with a set of clock-glasses having suitable openings for the electrodes. For the purpose of a separation, the current is usually started at about 3–4 amperes, and the potential of the auxiliary electrode noted. As a rule, this is only slightly above the equilibrium potential. The current is then regulated so that the potential of the electrode may remain constant. When no side-reactions take place, the current falls to a small residual value (generally about 0·2 ampere), as the metal to be separated disappears from the solution. The auxiliary electrode is then allowed to rise 0·1–0·2 volt, according to the metal.

It is obviously a matter of great importance to know when all the metal has been deposited. Under the conditions just assumed, the amount deposited per unit of time may be taken as roughly proportional to the amount still in solution. This being so, it follows that the amount in solution will decrease in geometrical ratio during successive equal intervals of time. If we, therefore, make the safe assumption that the concentration of the metal has fallen to under 1 p.c. of its original value in the time during which the potential and the current have been brought to their final value, it is clear that by continuing the experiment half as long again, the concentration of the metal will fall to under 0·1 p.c., so that the deposition can be considered finished.

In cases where side-reactions occur, the current does not fall to zero, but it generally attains a constant value which allows it to be seen when all the metal has been removed. In certain cases this can be tested for chemically, and by continuing the experiment for about half as long again as this reaction demands, the metal may be safely assumed to have been deposited completely. This method may be adopted, for example, in the separation of lead from cadmium, the former being roughly tested for by sulphuric acid. If none of these methods is available, the metal must be deposited to constant weight, or else the separation must be carried out under very carefully defined conditions for a length of time proved by previous experiment to be more than sufficient.

Sand has simplified the apparatus necessary for the potential measurements by fitting all the apparatus required for the measurement of the electrode potential into a single box. Full particulars will be found in Trans. Faraday Soc. 1909, 162.

F. M. Perkin uses the apparatus depicted in Fig. 67 for working with graded potentials. The vessel containing the electrolyte has a tube fused into the side. Into this side tube the capillary end of the auxiliary electrode is inserted.

CLASSIFICATION OF THE METALS FOR ELECTRO-ANALYTICAL PURPOSES.

Most metals can be deposited satisfactorily at the cathode, particularly since the introduction of the mercury cathode and of the graded potential methods. Theoretically, by grading the potential, it should be possible to separate any one metal from another. Indeed, in many cases, this can be done, but there are cases in which the potential differences at which two metals can be deposited, that is to say, the minimum potential at which they will both be deposited, lie so close together that it is not possible to so adjust the conditions that a separation can be effected.

GROUP I.—Copper, silver, mercury, gold, palladium, rhodium, platinum, iridium, bismuth, antimony, tin, (arsenic), tellurium. These metals are more electronegative than the hydrogen electrode, and, consequently, can theoretically be deposited quantitatively from acid solutions.

GROUP II.—Cadmium, zinc, and indium. These metals are more electropositive than hydrogen, but, owing to the supertension of the hydrogen evolution in acid solution, it is actually possible to deposit them from weak acid solutions.

GROUP III.—Iron, nickel, cobalt. These metals are more electropositive than hydrogen, but, as the supertension of hydrogen is very low, these metals cannot be deposited completely from acid solutions. They can, however, be deposited from acid solutions if a mercury cathode is employed.

GROUP IV.—The metals of this group can either be deposited as oxides at the anode, or as oxides at the cathode. The group comprises the following metals: lead, thallium, manganese, chromium, molybdenum, uranium. Some of them can, however, be satisfactorily deposited as an amalgam on a mercury cathode.

GROUP V.—The metals of this group are the most strongly electropositive, and can only be deposited by using a cathode of mercury; but even then it is not possible in all cases to obtain a quantitative separation. The metals of this group are aluminium, glucinum, calcium, strontium, barium, magnesium, potassium, sodium, lithium, rubidium, cæsium.

GROUP VI.—These are all anions, and their estimation has been rendered possible mainly through the work of Edgar Smith, who completely deposits the metals by means of a mercury cathode and estimates the anions by titration or other appropriate method. The most important anions analysed by this method are F', Cl', Br', I', SO_4'', CO_3'', $Fe(CN)_6''''$, $Fe(CN)_6'''$, PO_4''', NO_3'.

It has not been found possible to analyse organic anions by electrolytic methods, because they are either decomposed or various reactions more or less complicated take place. Thus, for example, when the acetate anion is given up at the anode, ethane is produced, which, of course, is given off in the form of a gas.

Nature of Deposit.

Sand (Trans. Chem. Soc. 1907, 383) has theoretically and practically worked out the conditions necessary for obtaining adherent metal deposits.

The production of a *uniform deposit* over the electrode depends entirely upon the relation between polarisation and the E.M.F. required according to Ohm's law to force the current from one part of the solution to the other (Zeitsch. Elektrochem. 1904, 452). The case of metals such as cadmium and zinc, which require a higher potential for their precipitation from most of their solutions than hydrogen, is a question of supertension. The metals can only be deposited by virtue of the supertension which is required to liberate hydrogen as a gas. This supertension varies with the material of the electrode, and may even vary at different parts of the same electrode, owing to different states of its surface. Consequently, it may happen that the metal is deposited on a portion of the electrode which has a high supertension, and will continue to grow there; but at rougher parts of the electrode, where the supertension is lower, hydrogen alone will be evolved. This is, for example, particularly noticeable in the case of zinc, which, instead of being evenly deposited over the surface of an electrode, apparently perfectly smooth and even, often comes out in patches, parts of the electrode being absolutely free from deposit. Some solutions also of the same metal appear to be more sensitive to variations in the quality and character of the electrode than others. Thus with ordinary electrodes when the potential is not graded, it is a matter of the greatest difficulty to obtain an adherent deposit of copper when the electrolyte is sulphuric acid. On the other hand, with electrolytes of potassium cyanide or nitric acid, an even deposit is readily produced.

The nature of the deposit.—Electrolytic deposits may be spongy, coarsely crystalline, or finely crystalline. The last is the only form in which metals may be deposited in order to yield satisfactory quantitative results. Sand considers (*l.c.*) that spongy deposits are most probably due to the metal being deposited in the form of an unstable hydride, which gradually decomposes with evolution of gas.

The difficulty of hydride formation is got over by keeping the potential of the electrode under control. Vigorous stirring of the electrolyte, small current density, and the presence of some oxidising agent, tend to keep the potential low. But, by using an auxiliary electrode and rapid rotation, it is possible to obtain metals from solutions from which, under ordinary circumstances, they cannot be deposited.

Copper.

Copper may readily be deposited from solutions which contain considerable quantities of nitric or sulphuric acid. But good deposits can also be obtained from cyanide solutions, and it is possible to employ solutions containing an excess of ammonia.

The solutions which give the best results are those containing nitric acid or potassium cyanide. Indeed, it is a matter of considerable difficulty to obtain satisfactory results in presence of free sulphuric acid, excepting when a mercury cathode is employed. For stationary work, either the gauze flag electrode or the cylindrical gauze electrode is to be recommended.

Nitric acid.—About 1 gram of the copper salt is dissolved in about 140 c.c. of water and 5–10 c.c. of nitric acid (sp.gr. 1·42) added to the solution; that is, from 8 to 10 p.c. of the acid. If the flag electrode is employed, usually about 120 c.c. of water is sufficient, in which case proportionately less nitric acid must be used. The solution may either be electrolysed at ordinary atmospheric temperature, or heated from 45°–50°; in the latter case the time required for the complete deposition of the metal is considerably lessened. The best C.D. to employ is from 0·8 to 1·2 amperes, when the E.M.F. will be from 1 to 2·8 volts. A bright red film will be seen to flash across the cathode almost immediately the circuit is completed. In cold solutions, from 2½ to 3 hours will be required to completely deposit the metal; with hot solutions the rate of deposition is considerably accelerated. To ascertain when the whole of the copper has been deposited, withdraw about 1 c.c. of the solution by means of a pipette, transfer to a test-tube, make alkaline with ammonia, then acid with acetic acid, and add a few drops of potassium ferrocyanide; the formation of a brown precipitate or colouration shows that there is still some copper left in the solution, in which case, of course, it is necessary to continue the electrolysis until, on further testing with the reagent, no colouration is produced.

If the electrolysis is run overnight there is a tendency to form nitrous acid owing to cathodic reduction. In such cases a small quantity of urea should be added and the electrolysis continued for about half an hour. Otherwise a portion of the copper remains in solution. The urea decomposes the nitrous acid.

Washing the deposit.—As the electrolyte contains an excess of free nitric acid in which the copper deposit is readily soluble, the washing has to be carried out with caution. Some workers prefer to siphon off the electrolyte without breaking the circuit, and to run in water at the same time, until the ammeter points to zero. The current is then cut off and the cathode removed, finally washed with distilled water and dipped into a beaker of absolute alcohol. It is then dried in the steam oven, and, after cooling for 20 minutes, weighed. When the gauze cylindrical electrode is used, a stoppered funnel as illustrated in Fig. 67 is very convenient.

The solution is drawn off until only about one quarter of the electrode is immersed. Distilled water is then run in, and the operations repeated until the ammeter shows zero. By operating rapidly, the cathode may be removed, and, if dipped at once into a beaker of water and then washed under the tap or in several changes of water and then in alcohol, absolutely accurate results can be obtained.

The deposit obtained from nitric acid is bright red, and generally has a more or less crystalline appearance. If the C.D. has been too high, it may be 'burnt,' and have a brownish appearance, and may be powdery and non-adherent. When it is desired to electrolyse over-night—and this is often found very convenient—a C.D. of from 0·2 to 0·3 of an ampere is used. It is generally advisable in this case to add more nitric acid, because, owing to the reducing action of the hydrogen liberated at the cathode, the nitric acid becomes converted into ammonia. This formation of ammonia causes the deposit to be spongy and of a bad colour, when it is difficult to wash and weigh. For running over-night about 2 c.c. extra of nitric acid should be added for every 100 c.c. of solution.

The deposits obtained with sulphuric acid are generally not satisfactory, but of all the copper deposits that obtained from solutions containing potassium cyanide is the most beautiful.

Potassium cyanide.—The colour of the deposited metal is pinkish red, and perfectly smooth. But, from other points of view, the deposition from cyanide solutions has no advantage over the deposits obtained from solutions containing nitric acid. The copper salt is dissolved in about 30 or 40 c.c. of distilled water, and then a freshly prepared solution of potassium cyanide added, until the precipitate first produced is dissolved. Slightly more potassium cyanide than is necessary to dissolve the precipitate should be used, but any considerable excess must be avoided. Generally speaking, from 1 to 1·5 grams of potassium cyanide should be used for every gram of copper salt taken.

The C.D. employed should be from 0·8 to 1·2 amperes. The E.M.F. required in cold solutions will be found to be about 5–6 volts; in warm solutions, from 4 to 5 volts. The whole of the copper is deposited in 2 to 2½ hours.

Rapid methods.—By employing rotating electrodes, either rotating anode or cathode, copper may be completely deposited in a few minutes. Thus Sand, by using his apparatus, was able to completely deposit the copper from 0·25 gram copper sulphate in 6 minutes, the number of revolutions of the anode per minute being about 800; in that of Fischer the copper from 0·3 gram copper sulphate was deposited in 10 minutes, the speed of revolution being 1000 to 1200. In the one case a rotating anode was employed and in the other the cathode was rotated. The electrolyte in both cases contained free nitric acid. Cyanide solutions give, however, equally satisfactory results.

Edgar Smith, by employing a rotating anode and mercury cathode, has deposited quantitatively 0·789 gram of copper in 10 minutes, and as much as 0·3945 gram per 4 minutes, the solutions containing sulphuric acid. The advantage of the mercury cathode is that almost any electrolyte can be employed equally satisfactorily. Indeed, the pure salt of the metal may be dissolved in water and electrolysed without the addition of any acid or other electrolyte. When the whole of the metal has been deposited, the solution is run off, and may then be titrated in order to determine the anion, *e.g.* SO_4''.

Silver.

Silver can best be deposited from solutions containing potassium cyanide. From solutions containing other electrolytes it is apt to be deposited in a crystalline feathery form, and consequently does not adhere well to the cathode. There is, however, a tendency for the results to be slightly too low when cyanide solutions are employed. It is very important that only the purest potassium cyanide be used in making up the solutions. For 0·5 gram of a silver salt about 3–4 grams of potassium cyanide will usually be found sufficient. With a C.D. of 0·5 to 1·0 ampere, and a temperature of 50°–60°, the silver will be deposited in from 1 to 2 hours. Using a cold solution and with a C.D. of from 0·2 to 0·35 ampere, the time required is from 4 to 4·5 hours. The deposit should either be washed by siphoning, or the electrode must be very rapidly removed from the electrolyte and dipped into water, in order to avoid loss by the solvent action of the potassium cyanide.

With rotating electrodes the silver can be deposited within a few minutes. By using an auxiliary electrode and rotating the anode vigorously, Sand was able to deposit silver from ammoniacal solutions in 7 to 8 minutes.

Smith, by using a mercury cathode and rapidly rotating anode deposited 0·2240 gram of silver from silver nitrate in 4 minutes. At the commencement of the operation an anodic deposit of silver peroxide was obtained, but after a minute or two this disappeared.

Mercury.

Many methods have been devised for precipitating mercury on platinum cathodes, and some of them give quite satisfactory results. When mercury is deposited on a platinum dish, or on a wire gauze electrode, it spreads evenly over the surface as a thin metallic film, which, however, is inclined to run together as the amount of mercury on the electrode increases in quantity. After the mercury has been deposited, the electrode is washed with water in the usual way, then in absolute alcohol, and finally in absolute ether. The last traces of ether may be removed by blowing dry air on to the electrode.

On no account may the mercury-coated electrode be heated. If the electrode is washed once in 90 p.c. alcohol, and then placed in a beaker of anhydrous acetone for a minute, it may then be dried without using ether. It is always advisable, before weighing, to place the electrode in a desiccator for 20 minutes. The desiccator should have a dish in it containing a little metallic mercury, because even at ordinary temperatures mercury volatilises to a small but appreciable extent.

The mercury can be removed from the electrode by heating in the Bunsen flame, but owing to the tendency for electrolytically deposited mercury to alloy with platinum, the electrode is almost invariably marked with black stains, and a slight loss in weight takes place. For this reason some workers prefer to plate the electrode with copper or silver before using. These difficulties are, however, entirely eliminated by using a mercury cathode; in fact, it is strongly recommended to employ always a mercury cathode when dealing with mercury.

Many electrolytes have been suggested, and all give more or less satisfactory results. Thus, the mercury salt may be dissolved in water and electrolysed in presence of a small quantity of sulphuric, hydrochloric, or nitric acid. With sulphuric acid, from 1 to 2 c.c. of the concentrated acid are added to each 100 c.c. of solution, and electrolysis conducted with a C.D. of 0·3–0·8 ampere per square decimeter, which is finally increased to 1 ampere towards the end of the operation. With rotating electrodes, currents of from 4 to 6 amperes per square decimeter may be employed. The temperature of the electrolyte may be 50°–60°, but not higher.

Sometimes, owing to the reducing action of the hydrogen given off at the cathode, mercurous salts are precipitated. The addition of small quantities of ammonium persulphate will cause them to go into solution again. The conditions with the other acids mentioned are very similar to those required for sulphuric acid. Potassium cyanide is not to be recommended, owing to slight solution of the anode taking place.

Sodium sulphide gives very satisfactory results, but care must be taken to employ a very pure solution of salt. From 25 to 30 c.c. of the concentrated solution of sodium sulphide are required for every 100 c.c. of solution. The solution should be heated to about 65°, and for stationary electrodes a C.D. of 0·15–0·25 ampere per square decimeter used. With rotating electrodes from 3 to 6 amperes per square decimeter may be used.

With mercury electrodes rotating anodes are almost invariably used, and high-current densities can be safely employed. The whole of the mercury can be deposited in from 15 to 25 minutes.

Cinnabar may be dissolved in *aqua regia*, the solution evaporated to dryness. The residue is then taken up with water, filtered from gangue, and then directly electrolysed after the addition of a small quantity of nitric acid.

Gold.

Gold may be deposited from its solution in cyanide or in sodium or potassium sulphide, or in ammonium thiocyanate. The drawback to using potassium cyanide is the tendency for the anode to go into solution. But with low-current densities, this only takes place to a small extent. The solution is made up by adding rather more than the quantity necessary of potassium cyanide to bring the gold salt into a clear solution. With stationary electrodes a C.D. of 0·6–0·8 ampere is employed at a temperature of 50°–60°, the metal being deposited in the course of 2 to 3 hours. With rotating electrodes a current of about 3 amperes may be employed, when the metal will be deposited in about 30 minutes.

Sodium sulphide.—From 20 to 25 c.c. of a saturated solution of sodium sulphide are used for every 100 c.c. of solution. With a C.D. of from 0·1 to 0·3 ampere the metal will be deposited in from 4·5 to 5·5 hours. With rotating electrodes and high-current densities, the results are too high, owing to deposition of sulphur along with the gold.

Ammonium thiocyanate.—5 to 7 grams of ammonium thiocyanate are dissolved in about 80–90 c.c. of water at 70° to 80°, and the gold solution run slowly in with constant stirring. The clear solution is electrolysed at a temperature of 40°–50° with a C.D. of 0·2–0·55 ampere, the metal being deposited in from 1·5 to 2 hours. This method has not been tried with rotating electrodes. The precipitation of small quantities of yellow canarine in the electrolyte during electrolysis does not interfere with the reaction.

E. F. Smith obtains good results by electrolysing a gold chloride solution, using a mercury cathode. In order to prevent the chlorine evolved attacking the anode, from 10 to 12 c.c. of toluene are added. The time required to deposit 0·15–0·2 gram of gold is about 5 to 7 minutes.

Most solvents for gold will also attack the platinum cathode. *Aqua regia*, for example, cannot be used to dissolve the gold from the platinum. F. M. Perkin recommends a dilute solution of potassium cyanide to which is added 4–5 c.c. of hydrogen peroxide, or from 2 to 3 grams of an alkali persulphate. On gentle warming the deposit is removed in a few seconds.

$$2Au+4KCN+H_2O_2=2KAu(CN)_2+2KOH.$$

Platinum.

Like gold, platinum can be deposited from solutions containing free mineral acids, but unlike gold, which from these solutions is deposited in a non-adherent form, it may be deposited with very feeble currents in a hard and reguline condition. With high currents and with stationary electrodes the metal is always deposited as platinum black. With a current of from 0·01 to 0·05 at a temperature of 50°–60°, about 0·1 gram of platinum can be deposited in 4·5 to 6 hours. Julia Langness (J. Amer. Chem. Soc. 1907, 459), by using a rotating cathode, deposited 0·2 gram of platinum from a solution of K_2PtCl_6 in 5 minutes. But the current, 17 amperes, must be looked upon as excessive for analytical purposes.

Before depositing platinum it is advisable to coat the cathode with silver.

Rhodium.

This metal may be deposited on to a silver-coated electrode from solutions acidified with phosphoric acid. A current of 0·18 ampere is used. As the process continues, the purple colour of the solution gradually disappears and becomes colourless, when the deposition is finished. With a rotating anode the metal may be deposited from solutions weakly acidulated with sulphuric acid in about 15 minutes with a current of 8 amperes, and with a current of 14 amperes in 5 minutes. The deposited metal has a black colour, but is quite adherent.

Palladium.

In order to obtain a dense and firmly adhering deposit of this metal from acid solutions, it is, according to Amberg (Zeit. f. Elektrochem. 1904, 386, 853, and Annalen, 1905, 235), necessary that the potential should not exceed 1·25 volts. With stationary electrodes the process is very slow, and polarisation at the anode takes place, owing to the formation of oxy- compounds. On the other hand, by using a rotating electrode and solutions of palladium ammonium chloride with 30 p.c. by weight of sulphuric acid and a C.D. of from 0·23 to 0·50 ampere, as much as 0·3–0·9 gram may be deposited in from 3·5 to 5 hours.

Julia Langness, by using currents of from 15 to 17 amperes, and an ammoniacal solution, has obtained quantitative deposits in from 3 to 5 minutes.

Antimony.

This metal may be deposited from its thiosalts, particularly sodium thioantimonite, a method originally suggested by Classen. During the electrolysis there is, however, a danger, owing to the deposition of sulphur at the anode, for sodium thioantimoniate to be formed, and this prevents the quantitative deposition of the metal. A. Fischer (Ber. 1903, 2474) recommends the addition of potassium cyanide to the electrolyte, which prevents the formation of the thioantimoniate, thus:

$$N_2S_4+3KCN=3KCNS+Na_2S.$$

There is one difficulty when sodium sulphide is used—the results obtained are usually slightly too high. This is due to the occlusion of small quantities of sulphur along with the metal. For this reason large quantities of metal should not be deposited by this method. The antimony salt is dissolved in 60–80 c.c. water made just alkaline with sodium hydroxide, any precipitate being ignored, then 20–25 c.c. of a fresh saturated solution of sodium sulphide added, and 2·5–3 grams of potassium cyanide. The solution is then electrolysed at from 30°–40°. With stationary electrodes the metal is deposited in from 4·5 to 6 hours; when rotating electrodes are used, in 30 to 45 minutes.

F. M. Perkin and H. D. Law (Trans. Faraday Soc. *i.* 262) recommend neutral tartrate solutions. The antimony salt is dissolved in water, and from 8 to 10 grams of ammonium tartrate added; if necessary, the solution is neutralised with dilute ammonia. At a temperature of from 70° to 80°, and a C.D. of 0·25–0·55 the metal can be deposited with stationary electrodes in from 2·5 to 3 hours.

Sand (Chem. Soc. Trans. 1908, 1572) dissolves the metal in 20 c.c. of hot conc. sulphuric acid, and dilutes the cold solution to 80 c.c. The solution becomes turbid owing to hydrolysis, but this disappears during the electrolysis, and does not affect the result. The auxiliary electrode potential is kept at from 0·55 to 0·65, but may be increased to 0·75 toward the end of the process. The time required to deposit 0·35–0·45 gram of metal is from 20 to 35 minutes with an anodic rotation of about 800 revolutions per minute. Small quantities of hydrazine sulphate (0·5–0·6 gram) are added to reduce any antimonial salts which may be formed.

Bismuth.

Until the advent of rotating electrodes, and particularly of the method of graded potential, bismuth was one of the most difficult metals to deposit, since it almost invariably came down in a powdery and non-adherent form. These remarks do not apply to the mercury cathode. According to Kollock and Smith (J. Amer. Chem. Soc. 27, 1539) to a solution containing about 0·2 gram of the metal as nitrate, the volume of which should not exceed 12 c.c., 0·5 c.c. of strong nitric acid is added. A current of about 4 amperes is passed, and the whole of the bismuth will be precipitated in from 12 to 15 minutes. The anode should be very rapidly rotated, so that the mercury may take up the bismuth as it separates, otherwise it may collect in a black mass beneath the anode.

Sand (Chem. Soc. Trans. 1907, 373) uses a solution containing tartaric acid; any excess of nitric acid, which may be in the original solution, is removed by the addition of sodium tartrate. By means of the auxiliary electrode, the cathode potential is maintained between 0·63 and 0·9 volt. The anode is rotated at 800 revolutions per minute. In one case the amount of metal in the solution was 0·2 gram, 2·5 c.c. of nitric acid (1:4) was added, and 8 grams of sodium tartrate. With a current varying from 0·2 to 3 amperes the metal was deposited in 9 minutes.

A. Fisher uses an electrolyte containing for each 0·5 gram metal, 10 grams of potassium oxalate, and 5 grams of Rochelle salt. By means of an auxiliary electrode, the cathode potential is kept at 0·8 volt. Temperature of solution, 75°; time required, 11 to 15 minutes.

Tin.

Tin can be satisfactorily deposited from an ammonium sulphide solution. Sodium sulphide is not satisfactory; indeed, tin is not thrown out from strong solutions at all. Hence, we have here a method of separation of antimony and tin. If the tin solution is acid, it is first neutralised with ammonia, and then sufficient yellow ammonium sulphide is added to dissolve the precipitate and form a clear solution. With stationary electrodes and a current of 1·0–1·8 amperes, the tin will be deposited in from 3 to 4 hours.

With rotating electrodes the metal can be deposited in from 15 to 35 minutes, depending upon the current employed, and the temperature of the electrolyte. Currents of from 1·8 to 8 amperes have been successfully employed.

A mercury cathode also gives very good results. The tin salt is dissolved in dilute sulphuric acid, and electrolysed with a current of from 2 to 5 amperes. From 0·5 to 0·8 gram can be deposited in from 8 to 12 minutes.

When platinum electrodes are employed, considerable difficulty may be experienced in removing the deposit. The simplest method is to make the electrode on which is the deposit, the cathode in dilute sulphuric acid, a piece of copper wire serving as cathode. Some workers prefer to coat the electrode with copper, and then the copper with tin, the tin being deposited from an ammonium oxalate solution; this proceeding, however, is tedious.

Tellurium.

Finely powdered tellurium is dissolved in a few c.c. of conc. sulphuric acid. The white anhydride so obtained is washed with a little freshly boiled water into the electrolysing vessel, and then 80 c.c. of a 10 p.c. solution of pyrophosphoric acid or sodium pyrophosphate added. The solution is then electrolysed with a C.D. of 0·1 ampere. Time of deposition, 4 to 5 hours When a rotating electrode is employed, the time of deposition is much accelerated.

GROUP II.—**Zinc.**

Zinc is rather a difficult metal to deposit satisfactorily and quantitatively, and a very large number of methods have been suggested by different workers. Although it is +0·77 volt more positive than hydrogen, it can be deposited from slightly acid solutions, owing to the high supertension of hydrogen evolution from the surface of zinc, the supertension of hydrogen being 0·70 volt.

With zinc it is advisable always to employ rotating electrodes. The electrodes need not, however, be made of platinum; nickel, particularly in the form of gauze, answers equally well.

Price and Judge (Trans. Faraday Soc. 1907, 88) use an electrolyte containing sulphuric acid which must not be more than $\frac{1}{6}N$ and sodium sulphate.

It is, in fact, better to keep the normality of the acid rather lower than one-sixth. By starting with a C.D. of 0·25 ampere and increasing to 2·0 amperes about 0·2 gram of metal can be deposited in 40 minutes.

Owing to acetic acid being much less dissociated than sulphuric acid, solutions containing considerable quantities of this acid may be used. Thus, Exner (J. Amer. Chem. Soc. 1903, 896) deposited 0·25 gram zinc with a current of 4 amperes in 15 minutes. The electrolyte contained 3 grams sodium acetate and 0·30 p.c. acetic acid. A. Fischer (Chem. Zeit. 1907, 25) takes 1 c.c. conc. sulphuric acid, 3·5 c.c. conc. ammonia, 1·5 c.c. acetic acid, and 2·5 grams ammonium acetate. A. Classen (Quant. Analyse d. Elektrochem. 1897, 156) uses a solution of potassium oxalate, the zinc solution is added to a solution of from 4 to 5 grams of potassium oxalate. As soon as the electrolysis has started, it is advisable to add a few c.c. of a 1 p.c. solution of oxalic acid. Ammonium salts must be absent.

Kollock and Smith use a mercury cathode, and a solution of zinc sulphate or zinc sulphate acidified with sulphuric acid.

Zinc adheres somewhat firmly to platinum electrodes, and, if left on for some time, seems to alloy with the electrodes. If, however, it is removed shortly after the electrolysis, no ill effect is produced. The best method to remove the deposit is to warm the electrode in a strong solution of sodium hydroxide.

Cadmium.

Although cadmium is electropositive to hydrogen by as much as 0·42 volt, yet, owing to the high supertension of hydrogen with this metal, it is possible to deposit it from acid solutions. Owing, however, to the depolarising action of nitric acid, nitrates should not be present; on the other hand, small amounts of chlorides do not seem to matter.

Cadmium may be deposited from solutions containing small quantities of free sulphuric acid. It is usually advisable to add, after the bulk of the cadmium has been deposited, the equivalent amount of sodium hydroxide to neutralise the sulphuric acid which has been set free through the deposition of the metal. In 100 c.c. of solution, 1 c.c. of concentrated sulphuric acid may be added before commencing the electrolysis. With stationary electrodes and a current of 0·1 to 0·35 ampere, the metal is deposited in from 3 to 4 hours; with a rotating electrode and a current of 4 to 5 amperes, the deposition is complete in 20 minutes. The deposition from cyanide solutions is the simplest and most easy to carry out. A solution of potassium cyanide is added to the cadmium solution until the precipitate first produced is dissolved, and then about half the quantity already added is run in. It is advisable also to add about 2 c.c. of a normal solution of sodium hydroxide. With stationary electrodes and a current of 0·15–0·35 ampere at a temperature of 50°, the deposit is complete in from 4·5 to 5·5 hours; with rotating electrode and a current of from 5 to 8 amperes, in from 15 to 30 minutes.

Group III.—Iron.

It is not often that the analyst requires to deposit iron electrolytically, owing to the very satisfactory methods of titration and precipitation. Iron cannot be deposited from acid or even from neutral salt solution upon a platinum electrode, owing to its being so much more electropositive than hydrogen—0·34 volt, while the supertension of hydrogen is only 0·08 volt. Kollock and Smith (Proc. Amer. Phil. Soc. 44, 149, and 45, 261) have, however, succeeded in depositing iron from weak acid solutions by means of a mercury cathode, the iron as it is deposited amalgamating with the mercury. The method described by these authors is as follows:—

Five c.c. contained 0·2075 gram of iron. Three drops (40 drops = 1 c.c.) of concentrated sulphuric acid were added to it, when it was electrolysed with a current of 3 to 4 amperes and 7 volts. The anode made from 500 to 900 revolutions per minute. The iron was completely deposited in 7 minutes. The water was then siphoned off and the amalgam washed, as in all previous cases, with alcohol and water.

From its oxalate, tartrate, or citrate solutions, iron may be satisfactorily deposited, but in all cases traces of carbon are deposited along with the metal. By employing low-current densities, the amount of carbon deposited from oxalate and tartrate solutions is negligible, but from citrates the results are almost always considerably too high.

Ammonium oxalate.—This method was first suggested by Classen (Zeit. f. Elektrochem. i. 288), and is the one most generally employed. The iron solution, which should be free from chlorides and nitrates, must be poured into the solution of ammonium oxalate, if it is in a ferrous condition, otherwise a precipitate of ferrous oxalate may be formed which is difficult to dissolve. With ferric salts the order of adding does not matter.

Dissolve 5–7 grams of ammonium oxalate or acid ammonium oxalate in a small quantity of hot water, and to this add the iron salt also dissolved in a little water. The solution is then made up to the required bulk, and electrolysed with a C.D. of from 0·6 to 1·2 amperes. Time of deposit from cold solutions and with stationary electrodes, 4 to 5 hours; from solutions at 50°–60°, in 2 to 2·5 hours. As the electrolysis proceeds, it will sometimes be noticed that a small quantity of ferric hydroxide separates. This is due to the solution becoming slightly alkaline, owing to the decomposition of the oxalate by the current. Should the hydroxide be thrown out, small quantities of oxalic acid must be added.

With rotating electrodes the time of electrolysis is from 14 to 20 minutes.

With tartrate solutions the results are equally good. The method of procedure is similar to that described for oxalates, ammonium tartrate being used in place of the oxalate. The advantage of the tartrate method is that ferric hydroxide is never deposited; consequently, it is not necessary to add tartaric acid, and thus less attention is required.

Nickel.

Nickel and cobalt are difficult to determine by general analytical methods, but they can both be readily and accurately analysed by electrochemical means.

Although many methods have been suggested for the deposition of nickel, few of these are of practical importance. Most of them depend upon the use of the salts of organic acids. In such cases there is a tendency for traces of carbon to be deposited with the metal. The most useful and generally applicable method for depositing nickel is that of Fresenius and Bergmann (Zeit. f. Anal. Chem. 33, 9), in which the double salts of potassium and nickel or ammonium sulphate together with excess of ammonia are used.

The nickel salt is dissolved in water and mixed with an aqueous solution of from 4 to 5 grams of ammonium sulphate, and from 30 to 35 c.c. of strong ammonia. If more than 1 gram of the nickel salt is employed, larger quantities of ammonia should be added. As, however, large quantities of strong ammonia are apt to contaminate the atmosphere, it is better to work with smaller quantities of nickel. Nitrates should be absent, as their presence considerably retards the rate of deposition. With a current of 1–1·5 ampere per sq. dcm., the metal will be deposited in from 2 to 2·5 hours; at a temperature of 50°–60°, the time will be from 1·5 to 2 hours; with rotating electrodes, in from 15 to 30 minutes, depending upon the conditions and the form of apparatus. The metal is usually deposited as a brilliant plating on the electrode. The deposit is at times somewhat difficult to remove, and, owing to its appearance being rather like polished platinum, it is not always easy to ascertain whether it has been completely dissolved off. The best method of removing the metal is to warm the electrode in moderately strong sulphuric or nitric acid.

Other methods employed are the double oxalate method of Classen and Von Reiss (Ber. 14, 1622); ammonia and ammonium borate, by F. M. Perkin and W. C. Prebble (Trans. Faraday Soc. 1904, 103). Kollock and Smith (Proc. Amer. Phil. Soc. 45, 262) have used a mercury cathode successfully, the time of deposition being from 7 to 20 minutes. An amalgam of 40 grams mercury and 1 gram nickel has the consistency of soft dough, and is bright in appearance.

Cobalt.

Cobalt may be deposited from an ammonium sulphate, ammonium hydroxide solution similar to that used in the case of nickel. But as a rule the results obtained are too low, owing to the tendency for peroxide to be formed on the anode.

F. M. Perkin and W. C. Prebble (Trans. Faraday Soc. 1905, 103) use a solution containing dihydrogen sodium phosphate and phosphoric acid. The solution is made up by adding 2 c.c. of a 5 p.c. solution of phosphoric acid to the solution of the cobalt salt in 70–80 c.c. water and then 20–25 c.c. of a 10 p.c. solution of dihydrogen sodium phosphate. The electrolysis should be commenced cold with a current density of 0·2–0·3 ampere per sq. dcm.; after about 50 minutes the solution is warmed to 50° or 60°, and the current increased to 1·2 ampere. If, as often happens, some peroxide is deposited on the anode, it can be removed by the addition of 0·2–0·3 gram of hydroxylamine sulphate. After the solution has become colourless, about 1 c.c. of *N*/1-ammonia should be added. The time necessary with stationary electrodes is from 4 to 5 hours. The deposit is extremely bright, resembling polished platinum.

The only methods which have been tried with rotating electrodes are solutions containing ammonium acetate and solutions with sodium formate. With currents of 8 amperes, L. Kollock and E. F. Smith (J. Amer. Chem. Soc. 29, 797) succeeded in depositing 0·3 gram of cobalt in from 30 to 40 minutes.

Group IV.—Lead.

Owing to its ready oxidisability, it is difficult to deposit lead satisfactorily on the cathode. Except in cases of separation from other metals, indeed, it is of no advantage to deposit it at the cathode. Sand has, however, found it a convenient method to separate lead from cadmium and bismuth (Chem. Soc. Proc. 22, 43).

From dilute solutions of nitric acid lead is partially deposited as metal on the cathode, and partially as peroxide at the anode. It is therefore necessary to have about 20 c.c. of nitric acid (1 : 4) to every 100 c.c. of electrolyte. Arsenic, manganese, selenium, and bismuth should be absent, and according to Vortmann (Annalen, 351, 283), antimony, silver, mercury, zinc, iron, cobalt, aluminium, and the alkali metals also cause the results to be high. Chromic acid should also be absent, and phosphoric acid retards the deposition. The lead salt is dissolved in water, and from 25 to 30 c.c. of strong nitric acid added. The electrodes used, whether stationary or rotating, should be roughened by the sand blast. With stationary electrodes and a current of from 1·3 to 1·8 ampere at a temperature of 60°–70°, the deposition will be complete in from 1 to 1·5 hours. At the commencement of the electrolysis a yellowish deposit is obtained which becomes orange or red, and finally dark-brown or black.

With rotating electrodes, the time of deposition is from 10 to 25 minutes.

At the end of the electrolysis the electrode is well washed by placing it in hot water, then washed with alcohol and ether, and heated to 220° in the air-bath for an hour. It must be cooled in a desiccator; the weight of the deposit is multiplied by the factor 0·866.

The best method to remove the deposit from the electrode is to warm it with equal volumes of nitric acid and water to which 4–5 grams of glucose has been added.

Lead does not give satisfactory results with a mercury cathode.

Manganese.

Manganese can only be deposited as oxide at the anode. It is, however, much more difficult to deal with than lead, as the deposit is apt not to adhere well. It is absolutely essential to employ roughened electrodes. Mineral acids cannot be employed. The most satisfactory electrolyte is one containing ammonium acetate, and Engels (Zeit. Elektrochem. ii. 413) has shown that the addition of small quantities of chrome alum helps to cause the deposit to adhere more firmly, probably owing to a depolarising effect. The manganese salt is dissolved in 40–50 c.c. of water, 8–10 grams of ammonium acetate added, and the solution electrolysed at a temperature of 75°–80°, with a current of 0·6 to 1 ampere. The deposition will be complete in from 1·5 to 2 hours.

With rotating electrodes the time will be about 30 minutes. In this case it is as well to add 10 c.c. alcohol to prevent frothing (J. Koster, Zeit. f. Elektrochem. 10, 553).

The best way to ascertain if all the manganese has been deposited, is to employ the permanganate test. Withdraw 1 or 2 c.c. of the solution, add 3 c.c. conc. nitric acid, and about 1 gram of red lead. Boil for a minute or two and dilute. A pink colouration indicates that the whole of the manganese has not been removed.

When all the manganese has been deposited, the electrode is washed as usual, and then strongly heated in order to convert the hydrated manganese peroxide into trimanganese tetroxide Mn_3O_4. It is necessary to heat until the black deposit becomes a dull orange red. The weight of the deposit multiplied by 0·72 gives the weight of metallic manganese.

Chromium.

This metal cannot be deposited on the anode as peroxide; neither under ordinary conditions is it possible to obtain a cathode deposit. Kollock and Smith (Trans. Amer Chem. Soc. 27, 1905, 1255) have succeeded in depositing it in the form of an amalgam by employing a mercury cathode. The electrolyte consisted of dilute sulphuric acid. With a current of 1–3 amperes 0·12 gram was deposited in 20 minutes. This method is useful for separating chromium from aluminium, which latter metal is not deposited as an amalgam.

Classen (Ber. xxvii. 2060) oxidises chromic salts to chromates in an ammonium oxalate solution. This method is useful for separating chromium from iron, nickel and cobalt, and in the analysis of chromium steels and of chrome iron ore. The chromic acid produced can be estimated iodometrically or by precipitation as lead or barium chromate.

The solution containing the iron and chromium salt has excess of ammonium oxalate added to it, and if free mineral acid is present is neutralised with ammonia. It is then electrolysed, when the iron is deposited at the cathode and the chromium oxidised to chromate. The iron, when deposited in presence of chromium salts, is usually very brilliant like polished platinum. When all the iron is deposited, the solution is removed, the iron deposit dried and weighed, and the chromium determined. If the whole of the chromic salt has not been oxidised during the deposition of the iron, the solution is again electrolysed. By using a rotating anode it is possible to completely oxidise 0·15 gram of a chromic salt, such as $Cr_2(SO_4)_3$ or Cr_2Cl_6 in 90 minutes, the volume of the solution being 120 c.c. and the amount of ammonium oxalate 15 grams. The electrolyte should be heated to 80°, and a current of from 5 to 5·5 amperes employed (Elektronalytische Schnellmethoden, p. 180).

Uranium.

Uranium is deposited at the cathode as oxide from solutions containing acetic acid or ammonium carbonate. The deposit consists of $U_3O_4,3H_2O$. At the end of the operation this is heated strongly to convert it into U_3O_8.

Wherry and Smith (Trans. Amer. Chem. Soc. 29, 806), by using a rotating cathode and an electrolyte containing in 125 c.c. 2·5–5·5 gram sodium acetate, deposited 0·25 gram of uranium in from 15 to 30 minutes, the current employed being 3–5 amperes, the electrolyte being either cold or heated to 50°.

Molybdenum.

From solutions containing dilute sulphuric acid, molybdenum can be deposited as peroxide at the cathode, but the deposit cannot be weighed as such. Wherry and Smith (Trans. Amer. Chem. Soc. 29, 806), therefore, oxidise it by means of nitric acid and weigh as MoO_3.

Thallium.

Many methods have been suggested for the electrolytic analysis of thallium, but only one can be considered satisfactory, and that is, by using a mercury cathode. By depositing the metal into pure mercury, it is found that portions are lost on weighing; but if the mercury contains a small quantity of zinc, this is not the case. Smith recommends to deposit the zinc and mercury simultaneously. In order to do this a definite volume of zinc sulphate solution of known strength is added to the solution before electrolysis. The electrolyte consists of dilute sulphuric acid. The amount of zinc necessary to protect the thallium is very small, and need not be more than 0·001 gram. With a current of 5 amperes it is possible to deposit as much as 0·2 gram in about 10 minutes. It is, however, advisable to electrolyse for a longer time.

GROUP V.—**Sodium.**

E. F. Smith (Trans. Amer. Chem. Soc. 25, 1903, 890) was the first to show that the metals of the alkali group could be analysed electrolytically. The method is based on the removal of the halogen anion of the metal by causing it to unite with silver, the alkali metal remaining in the solution as hydroxide is determined by titration; by ascertaining the increase in weight of the silver anode, the halogen can be also determined.

An ingenious apparatus has been devised by Hildebrand (Trans. Amer. Chem. Soc. 29, 1907, 447) for the analysis of the cations of the alkali metals, and of barium and strontium; and at the same time of various anions. In principle the cell resembles that of the Castner-Kellner process employed in the manufacture of sodium hydroxide.

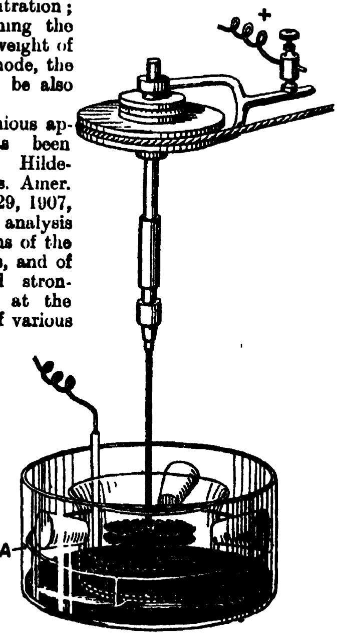


FIG. 68.

The outer cell (Fig. 68) consists of a crystallising dish, 11 cm. in diameter and about 5 cm. deep; a beaker 6 cm. in diameter and 4·5 cm. high, with the bottom cut off, is placed inside and rests on a triangle of glass rod placed on the bottom of the crystallising dish. The beaker is kept in position in the middle of the dish by means of three rubber stoppers fitted radially between it and the outer dish. Two compartments are thus formed, which are sealed off by means of mercury. In the outer compartment there is a ring consisting of six turns of stout nickel wire, provided with three legs dipping into the mercury and serving to maintain the lowest winding of the nickel about 1 cm. above the surface of the mercury, when sufficient is placed in the dish to seal off the two compartments. By means of a platinum wire passing through a glass tube the mercury is made the cathode. The anode consists of two discs of platinum gauze heavily plated with silver.

Pure mercury must be used, and the cell must be kept scrupulously clean. Before starting the cell, mercury is poured in so that its level is about 3 mm. above the lower edge of the inside beaker. The solution to be electrolysed is then put into the inner compartment. In the outer one enough distilled water to cover the nickel wire is placed, and to this 1 c.c. of a saturated solution of common salt. By this arrangement the amalgam formed in the inner compartment is immediately decomposed in the outer one. The sodium chloride serves merely to make the liquid a conductor, so that the action may proceed more rapidly at the commencement. Unless this is done, the amalgam is not entirely decomposed in the outer compartment, because pure water does not attack it rapidly enough to prevent the partial decomposition in the inside cell. After the electrolysis is complete, the entire contents of the cell are poured into a beaker, the cell rinsed, and the alkali titrated. After titration the mercury is washed, the water decanted, and the metal poured into a large separating funnel from which it can be drawn off clean and dry.

The annexed table gives the results which were obtained by Hildebrand.

The weighed gauze anode is clamped to the shaft. The latter is lowered into the cell till the lower gauze is about 5 mm. from the surface of the mercury. The most convenient speed for the motor is about 300 revolutions per minute. The anode does not require washing, as the water after electrolysis is pure. It may be at once dried in the steam oven.

Time: Mins.	Volts	Amperes	Sodium in grams		Chlorine in grams	
			Present	Found	Present	Found
30	4·0–2·5	0·50–0·02	0·0461	0·0459	0·0708	0·0704
45	3·5–2·5	0·34–0·01	0·0461	—	0·0708	0·0706
40	3·5–3·0	0·50–0·01	0·0461	—	0·0708	0·0704
45	4·0–3·5	0·65–0·01	0·0461	—	0·0708	0·0716
30	4·0–2·5	0·76–0·02	0·0461	—	0·0708	0·0713
55	3·0	0·26–0·02	0·0461	—	0·0708	0·0709

By means of this apparatus the halogen salts of the alkali metals can be analysed. Also the halogen salts of barium and strontium. In fact, any anion with any metal which will unite with silver to form an insoluble salt can be analysed, provided, of course, that the metallic salt is soluble, and that the metal will form an amalgam with the mercury. In the case of the alkali metals and of strontium and barium, the hydroxides of which are soluble in water, the cations are analysed by titration. With other metals forming amalgams which are not readily decomposed this method of analysis is not to be recommended, because, in the first place, the considerable quantity of mercury necessary is inconvenient to weigh, and, secondly, it requires to be kept very pure, consequently the continual purification of such large quantities of mercury would be tiresome.

Analysis of anions when united with heavy metals. The SO_4 anion in such salts as copper sulphate may be analysed by electrolysing a known weight of copper sulphate dissolved in water with a mercury cathode and a platinum anode as already described. When all the copper has been deposited, the solution is siphoned off, the amalgam washed with water, and the wash water added to the original solution. The whole of the anode solution is then titrated with *N*-sodium hydroxide. The copper can, of course, be estimated by weighing the amalgam.

Separation of sodium from calcium and magnesium. When calcium and magnesium salts are electrolysed in Hildebrand's apparatus, it is found that the hydroxides of these metals are precipitated in the inner cell. It has therefore been found possible to separate sodium from these metals by means of this apparatus. The outer cell contains all the sodium as hydroxide, and the sodium can be determined by titration. The analytical results obtained are practically theoretical.

In a similar manner barium can be separated from calcium and magnesium.

Arsenic.

It is not possible to deposit arsenic quantitatively in the metalloid condition, neither can it be precipitated at the anode as oxide. Arsenic is readily converted by nascent hydrogen into arseniuretted hydrogen, its gaseous hydride, AsH_3; hence, electrolytic methods of analysis are not usually employed for analysing arsenic compounds. It is, however, possible to estimate very small quantities of arsenic contained in food, &c., by electrolysis. The process consists in evolving electrolytic hydrogen in presence of the arsenic, whereby the arsenic is converted into arseniuretted hydrogen. The gaseous hydride is then passed through a glass tube, heated by a small Bunsen burner, as in the Marsh apparatus, whereby the arsenic is deposited upon the tube in the form of a mirror. In order to estimate the amount of the arsenic, the mirror is then compared with mirrors prepared from known quantities of arsenic.

In 1812 Fischer (Gilbert's Ann. 42, 92) suggested the employment of the electric current to detect the presence of very small quantities of arsenic. It was again suggested by Bloxam (Quart. Journ. Chem. Soc. 1861, 13, 12 and 338) in 1861, but the apparatus had several disadvantages, and never came into practical use. Since then various modifications have been suggested by different authors, and, in 1903, Thorpe (Journ. Chem. Soc. 1903) describes a new form of apparatus which has been successfully employed for the analysis of traces of arsenic in food, beer, and other substances. It consists of a platinum cathode hung in a glass cylindrical vessel, which is open at the end, and fits into a Pukal porous cell. The porous cell is surrounded by the anode, and stands in an outer vessel. The upper portion of the cylinder is open, and has a ground neck for the insertion of the drying tube filled with anhydrous calcium chloride, and also carries the funnel, which is fitted with a tap, through which the solution to be tested is run in. A capillary tube is connected to the end of the calcium chloride tube. The middle of this tube is heated by means of the small Bunsen burner, and is surrounded where the flame heats it with a piece of platinum or iron-wire gauze, to prevent the tube being fused. The whole apparatus is placed in a vessel containing cold water, to prevent undue heating during electrolysis.

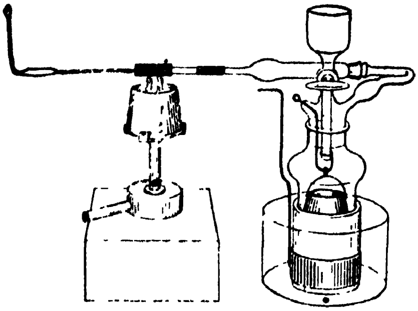


FIG. 69.

Method of working. The apparatus is carefully washed with distilled water. The outer cell E is filled with dilute sulphuric acid (30 p.c.), then the inner cell. (The porous cell should be soaked in dilute sulphuric acid for about half an hour before being used.) As soon as all the connections are made, the Bunsen burner is placed in position, but not lighted, and the current is passed. A current of about 5 amperes should be used; the escaping hydrogen thereby produces a flame of about 3 mm. in size. As soon as all the air has been driven out, which usually occupies about 10 minutes, the issuing hydrogen is ignited and the Bunsen burner lighted. If after about 15 minutes no brown ring makes its appearance, the reagents may be considered free from arsenic. At the end of 30 minutes the capillary tube is sealed off, and the open end also fused together. The mirror is then compared with the standard mirrors as above described.

Preparation of standard mirrors. Pure resublimed arsenious oxide is ground in an agate mortar and dried at 100°. Then 0·1 gram is carefully weighed and washed into a 1-litre flask, the flask being filled to the mark with distilled water. Each 1 c.c. of this solution contains 0·0001 arsenious oxide; 100 c.c. of this solution are diluted to 1 litre. This second solution contains 0·00001 gram of arsenious acid in each 1 c.c., or 0·01 mg. Standard tubes containing 0·004, 0·006, 0·008, 0·010, &c., mg. can then be prepared.

When foodstuffs are being examined for arsenic, Thorpe considers it advisable to take a portion of the foodstuff—arsenic free—and mix it with the known quantity of arsenic before proceeding to electrolyse it. The standard mirrors are thus prepared under the same conditions as those under which the suspected foodstuff is tested.

S. R. Trotman (J. Soc. Chem. Ind. 23, 177) recommends the adoption of a parchment membrane in place of the porous Pukal cell, as he considers this decreases the resistance, and thus makes the apparatus more sensitive. It is, however, not so convenient to use.

Sand and J. E. Hackford (Chem. Soc. Trans. 85, 1018) use the parchment membrane, but they also employ a heavy lead cathode and a lead anode. Their apparatus is thereby much cheaper than that used by Thorpe, and is said to be equally accurate.

Metallic Separations.

A large number of separations of metals by electrolytic methods have been worked out, but in many cases a purely chemical procedure or a combination of electrolytic and chemical methods is easier. There are, however, cases in which satisfactory and rapid electrolytic separations can be carried out. A few of the more important are given below.

Copper from nickel. By employing a rotating anode with an auxiliary electrode, and maintaining the cathode potential at 0·7–0·75 volt, copper can be deposited from solutions containing sulphuric acid. The solution is then made alkaline with ammonia, when the nickel can be deposited. If the cathode potential is not regulated, small quantities of the nickel are deposited along with the copper.

Exner (J. Amer. Chem. Soc. 25, 896) finds that by employing a solution containing nitric acid and ammonium nitrate (volume of solution 125 c.c.; HNO_3, 0.25 c.c.; 3 gram NH_4NO_3) and using a rotating anode, it is possible to deposit as much as 0·25 gram copper in 15–20 minutes; the nickel, which may be of equal weight, remains in solution, and can be afterwards deposited.

Copper from lead. Since lead is deposited from solutions containing nitric acid as peroxide on the anode, whilst copper is deposited as metal at the cathode, it might be supposed that there would be no difficulty in depositing both metals concurrently. It must, however, be remembered that unless there is a considerable concentration of nitric acid, a portion of the lead will be deposited as metal at the anode. On the other hand, in presence of copper, the tendency to reduction of the lead and its appearance at the cathode is decreased; that is to say, in presence of copper a lower concentration of nitric acid is required. It has, therefore, been found possible to separate the two metals. The volume of solution employed was 85 c.c., and contained 1 c.c. HNO_3 (1 : 4). With a rotating anode and a current of 2 amperes, the whole of the lead was deposited in 5 minutes. The current was then increased to 10 amperes, when the last traces of copper were removed. The washing and drying of the anode deposit requires care, since the peroxide when deposited from weak acid solutions does not adhere so well as from stronger solutions (Sand).

Copper and arsenic. McCay finds the following conditions give a satisfactory deposit of copper in presence of arsenic. The arsenic remaining in the solution cannot, however, be estimated electrolytically, unless present in very small quantities.

To the solution 20 c.c. ammonium hydroxide (sp. gr. 0·91) and 2·5 gram ammonium nitrate are added, the volume of solution being 125 c.c. The solution is then electrolysed at a temperature of 50°–60°, with 0·5 ampere per 100 sq. decm. of electrode surface. As much as 0·22 gram of copper will be deposited in 3 hours. With a rotating anode about 15 minutes are required. In this solution the arsenic should be present as arsenate. Copper and arsenic may also be separated electrolytically from solutions containing potassium cyanide. If acid, the solution is neutralised, and then sufficient potassium cyanide added to just redissolve the precipitate first produced. With a current 0·25–0·27 ampere, the whole of the copper is deposited in about three hours.

Antimony from tin. Tin can be quantitatively deposited from solutions containing excess of ammonium sulphide. It cannot, however, be deposited from solutions containing excess of sodium sulphide. Antimony, on the other hand, can be deposited from solutions containing excess of sodium sulphide. It is therefore possible to separate antimony from tin by adding excess of sodium sulphide to a solution containing the two metals. If the solution is acid, it is first made slightly alkaline with sodium hydroxide before the sodium sulphide is added. It is, however, better to first precipitate the two metals as sulphides, and then dissolve them in a concentrated solution of sodium sulphide. The tin should be in the stannic state. The solution is electrolysed at a temperature of 50°–60° with a current of from 0·2 to 0·9 ampere per sq. dcm. of electrode surface. In from 2 to 4 hours the whole of the antimony is deposited. It is, however, almost always contaminated with small quantities of tin.

In order to deposit the tin, the sodium sulphide must be decomposed. This is done by adding about 25 grams of ammonium sulphate, and boiling until no more hydrogen sulphide is evolved. The tin is now deposited by electrolysing with a current density of from 0·3 to 0·5 amperes.

The best method of separating antimony and tin is that of Sand, by means of graded potential and a rapidly rotating anode (Chem. Soc. Trans. xciii. (2) 1908, 1572). From solutions containing strong sulphuric acid (1 : 1) antimony is deposited at an auxiliary potential of 0·65 volt when the temperature is kept above 100°, and a small quantity of hydrazine sulphate is added. Tin, on the other hand, under similar conditions, is not deposited below 0·8 volt. The method of procedure when dealing with alloys of antimony and tin is as follows:—

The alloy is dissolved in a mixture of 40 c.c. conc. sulphuric acid, 5 c.c. water, and 2 c.c. nitric acid (1:42); on heating to 180°–200° solution rapidly takes place. It is necessary to remove the nitric acid because it causes the formation of antimonic acid, which is only slowly reduced to the metallic state electrolytically. In order to decompose the nitric acid (nitrosulphonic acid), a current of 5 amperes is passed, and the liquid heated to 250°–270°. After the current has been passed for 5 to 10 minutes at the high temperature, it is stopped. The solution is cooled to 100°, and 0·5 gram of hydrazine sulphate added. (N.B.—The amount of hydrazine sulphate added should be equal to the weight of metal taken.)

The temperature is then raised to 300°. It is again cooled to 100°, when from 30 to 40 c.c. of water and another 0·5 gram of hydrazine sulphate are added.

The anode [1] is then rotated to ensure mixing of the solution, the temperature of which rises to about 120°. The analysis is now begun, the auxiliary potential having first been adjusted to 0·53–0·65 volt. The current will vary between 3–4 amperes, and, at the end of the electrolysis, will drop to 0·4–0·5 volt. Time of electrolysis from 20 to 30 minutes.

The tin is determined as follows: The solution after the antimony has been deposited is mixed with about 4 grams of oxalic acid, and is neutralised with strong ammonia. In order to prevent loss by spurting the electrodes are placed in position, the rotating stem being passed through a hole drilled in a clock glass. The ammonia is poured on the clock glass and runs down the stem of the electrode into the solution, the anode or inner electrode being at the same time rotated. Considerable ebullition ensues, but none of the liquid is spurted out. Exact neutralisation is ascertained by the use of methyl orange as indicator. Litmus cannot be employed, since its colloidal nature hinders the deposition of the tin. After neutralisation, 0·5–0·75 c.c. of sulphuric acid are added for every gram of oxalic acid previously added.

The solution is electrolysed at a temperature of 70° with a current of 3–4 amperes. Time of deposit, 60–80 minutes.

Silver and copper. (Smith and Frankel, Amer. Chem. J. 12, 104.) To a neutral solution of the silver and copper salt, add 2–3 grams of pure potassium cyanide. Electrolyse at a temperature of 65° with a current of 0·03–0·05 ampere, and maintain the potential at 1·1–1·6 volt. The silver will be completely deposited in from 4 to 5 hours. After the silver has been weighed, the electrode is replaced, the current and voltage increased, when the copper will be deposited.

Silver may also be separated from copper in ammoniacal solutions by using an auxiliary electrode, and keeping the potential below 0·5 volt.

Iron from other metals. Iron can readily be separated from aluminium, vanadium, glucinum, uranium, thorium, and many other metals with which it may be alloyed by dissolving in sulphuric acid, filtering from any residue, nearly neutralising with ammonia, and electrolysing with a mercury cathode.

Cadmium from zinc. These metals can be separated by means of graded potential. The solution is made up by adding first 2 c.c. of conc. sulphuric acid, then 3·33 grams of sodium hydroxide, and 1 c.c. of glacial acetic acid. The auxiliary electrode is kept at a potential of 1·15–1·20 volts, and the solution electrolysed at a temperature of 30°. The whole of the cadmium will be deposited in 11–14 minutes. The potential is afterwards raised, when the zinc can be deposited in about 30 minutes.

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[1] After the metal has dissolved, the subsequent operations are carried out with the electrodes in position.

Bibliography.—Electroanalysis, by Edgar Smith (P. Blakiston's Son & Co., Philadelphia); Practical Methods of Electrochemistry, by F. Mollwo Perkin (Longmans, Green, & Co., London); Elektroanalytische Schnellmethoden, by A. Fischer (Ferdinand Enke, Stuttgart); Quantitative Analyse durch Elektrolyse, by A. Classen (Julius Springer, Berlin); Analyse des Métaux par Électrolyse, by A. Holland et L. Bertiaus (H. Dunod et E. Pinat, Paris); Developments of Electroanalysis, Fresenius, Zeitsch. Anorg Chem. 1913, 81, 4. F. M. P.

ANAMIRTA COCCULUS or **A. PANICULATA** (Colebr.). The former is the superseded name, and the latter the true name, of the Indian Menispermaceous liane, whose dried fruits (Grains of Paradise) are supplied under the name of *Cocculus indicus* (*v.* COCCULUS INDICUS).

ANAMIRTIN *v.* PICROTOXIN.

ANANAS, OIL or **ESSENCE OF.** A solution of ethyl butyrate in 8 to 10 times its weight of alcohol. It possesses the odour of the pineapple (*Ananas sativus* (Schult.)), and is employed in confectionery and perfumery; also to imitate the flavour of rum (Hofmann, Annalen, 81, 87).

ANANDONIS GREEN. *Hydrated chromium sesquioxide* (*v.* CHROMIUM).

ANASPALIN. Trade name for a form of wool-fat.

ANATASE or *Octahedrite.* One of the trimorphous forms of titanium dioxide (TiO_2) met with as crystallised minerals; the others being rutile and brookite. It is found as small, isolated crystals of a steel-blue or honey-yellow colour, in schistose rocks, particularly in the Alps; and as microscopic crystals is of common occurrence in sedimentary rocks. L. J. S.

ANCHIETA BARK. The root bark of *Anchietea salutaris* (A. St. Hil.), one of the Violaceæ, a bushy shrub growing at Rio de Janeiro. It contains *anchietine*, a substance crystallising in straw-coloured needles, having a nauseous taste. Used for syphilis and quinsy (Peckolt, Arch. Pharm. [2] 97, 271).

ANCHUSIN (*Alkannin*) *v.* ALKANNET.

ANCYLITE. A hydrated basic carbonate of cerium, lanthanum, and didymium, and strontium $4Ce(OH)CO_3 \cdot 3SrCO_3 \cdot 3H_2O$, found as small, yellow, orthorhombic pyramids with curved faces in syenite-pegmatite at Narsarsuk in the Julianehaab district, south Greenland; sp.gr. 3·95.

An allied mineral, with the formula

$$4(Ce,La,Di)_2(CO_3)_3 \cdot 5SrCO_3 \cdot (Ce,La,Di)_2O_2,$$

has been found as orthorhombic grains forming, with celestite, monazite, felspar, &c., a constituent of crystalline limestone at Ambatoarinina in Madagascar. This has been named ambatoarinite (A. Lacroix, 1916). L. J. S.

ANDA-ASSU, OIL OF. An oil obtained from the seeds of *Joannesia Princeps* (Vell.), belonging to the Euphorbiaceæ, growing in Brazil. It is clear, slightly yellowish, odourless, with a taste at first nauseating and then sweet. It solidifies at 8°, its sp.gr. at 18° is 0·9176 (Pharm. J. [3] 12, 380).

ANDALUSITE. One of the three modifications of crystallised aluminium silicate Al_2SiO_5, and belonging to the orthorhombic system; the other modifications being the minerals kyanite and fibrolite. Andalusite occurs in crystalline schists and metamorphic rocks, the variety chiastolite being specially abundant in the baked clay-slates surrounding intrusive igneous masses. It is also found as small crystals and grains in some granites, due probably to fragments of the surrounding slates having been incorporated in the igneous magma. Grains of andalusite are found in the sands and sedimentary rocks derived from these primary rocks. The pleochroism, from olive-green to rose-red, is a characteristic feature of the mineral under the microscope. D 3·18, H 7½. Large, rough opaque crystals are well known from Lisens-Alp in the Tyrol. Clear transparent pebbles of a rich brown colour are found in the Rio Jequitinhonha in Minas Geraes, Brazil; this material when cut as a gem-stone displays the strong pleochroism. The variety known as chiastolite shows in cross-sections of the prismatic crystals a dark cross of carbonaceous material enclosed in the lighter coloured andalusite; such material is cut as a gem-stone or charm. Large crystals of chiastolite have been found in considerable numbers at Bimbowrie, near Olary in South Australia. L. J. S.

ANDAQUIES WAX *v.* WAXES.

ANDESINE. A soda-lime felspar belonging to the group of plagioclase-felspars (*v.* FELSPAR). L. J. S.

ANDESITE. A group of volcanic rocks of intermediate composition, containing on an average 60 p.c. of silica, and corresponding to the plutonic diorites. They are usually dark-coloured, compact rocks, sometimes with a porphyritic structure or a vesicular texture; and are composed essentially of plagioclase-felspar with a ferromagnesian mineral, and sometimes a glassy base. According to the ferromagnesium mineral present, the varieties hornblende-andesite, biotite-andesite, and pyroxene-andesite are distinguished. When quartz is present the rock grades into the dacites. Sp.gr. 2·6–2·8. They are of wide distribution. The Andes of South America and the Cordilleras of Central and North America are built up largely of andesites; and here, as well as in Hungary, ore-deposits, particularly those of gold and silver, frequently occur in connection with them. In the British Isles they are abundant in the Midland Valley of Scotland, the Cheviot Hills, the Lake District, and in North Wales, and in these districts are quarried for road-stones. On the Continent they are also used for building stone and mill-stones. L. J. S.

ANDORITE. Sulphantimonite of silver and lead $AgPbSb_3S_6$, crystallising in the orthorhombic system. The mineral was independently described in 1892 from Felsőbanya in Hungary, and Oruro in Bolivia, under the names andorite, sundtite, and webnerite. It is dark steel-grey with metallic lustre, and a shining black streak; no cleavage; sp.gr. 5·35; H 3½. Analyses show 10–11·7 p.c. of silver (according to the formula Ag = 12·42 p.c.), there being small amounts of copper also present. At Oruro, in the San José and Itos Atocha mines, it occurs rather plentifully as well-formed crystals and as a massive silver ore (Prior and Spencer, Mineralog. Mag. 1897, xi, 286; Spencer, *ibid.* 1907, xiv, 316). L. J. S.

ANDROGRAPHIS PANICULATA (Nees) or

Karyat. An Indian plant; is used as a tonic, and is similar to quassia in its action.

ANDROPOGON OILS *v.* OILS, ESSENTIAL.

ANDROSIN *v.* GLUCOSIDES.

ANESIN (*Aneson*). An aqueous solution of acetonechloroform, having marked anæsthetic and hypnotic properties (Apoth. Zeit. 1897, 12, 608) (*v.* ACETONECHLOROFORM).

ANETHOL *v.* OILS, ESSENTIAL.

ANGELICA OIL *v.* OILS, ESSENTIAL.

ANGELINE $C_{10}H_{13}O_3N$ (surinamine, geoffroyine, andirine, rhatanine) (Hiller-Bombien, Arch. Pharm. 1892, 230, 513; Goldschmidt, Monatsh. 1913, 33, 1379; 34, 659), m.p. above 233° (indefinite). Identical with *n*-methyl-*l*-tyrosine $[\alpha]_D^{21}+19{\cdot}75°$. Synthesised by Fischer and Lipschitz (Ber. 1915, 48, 360).

ANGICO RESIN. A Brazilian gum obtained from *Piptadenia rigida* (Benth.) [*Acacia Angico*]; soluble in water and proof spirit. Used in chest complaints (Symes, Pharm. J. [3] 13, 213). Angico wood is that of another Brazilian leguminous plant, *Enterolobium ellipticum* (Benth).

ANGIONEUROSIN. Syn. for nitroglycerin as used in pharmacology.

ANGLESITE. Native lead sulphate ($PbSO_4$), forming brilliant, colourless, orthorhombic crystals, isomorphous with barytes ($BaSO_4$) and celestite ($SrSO_4$). It occurs in the upper oxidised zones of veins of lead ore, having resulted by the alteration of galena (PbS). It is less common than cerussite ($PbCO_3$), with which it has sometimes been mined as an ore of lead. Good crystals have been found at many localities, perhaps most abundantly at Broken Hill, in New South Wales. The mineral takes its name from the Isle of Anglesey, where crystals were found by W. Withering, in 1783, in the Parys copper-mine. L. J. S.

ANGOSTURA BARK or **ANGUSTURA BARK** *v.* CUSPARIA BARK.

ANHALAMINE, ANHALINE, ANHALONIDINE, ANHALONINE, *v.* MEZCALINE.

ANHALONIUM · **(CACTUS) ALKALOIDS.** Seven different bases have been isolated from various species of cactus and have been investigated chiefly by Heffter. They are derivatives of β-phenylethylamine. *Anhaline* is β-*p*-hydroxyphenyldimethylethylamine,

$$HO\,C_6H_4\,CH_2{\cdot}CH_2{\cdot}N(CH_3)_2$$

identical with *hordenine*. *Mezcaline* is β-3·4·5-trihydroxyphenylethylamine. *Anhalamine*, *anhalonidine* and *pellotine* are methylated 3·4·5-trihydroxyphenylethylamines, but *anhalonine* and *lophophorine* each contain two of their three oxygen atoms in a different kind of linking (E. Späth, Monatsh. Chem. 1919, 40, 129).

ANHYDRITE. A mineral consisting of calcium sulphate $CaSO_4$, so named to distinguish it from the more common hydrated calcium sulphate, gypsum. From a pure aqueous solution calcium sulphate crystallises as gypsum, but when the solution is highly charged with salts (sodium, potassium, and calcium chlorides, and magnesium sulphate) it separates as anhydrite. Anhydrite crystallises in the orthorhombic system, but in its crystallographic characters it shows little analogy with the orthorhombic barium and strontium sulphates, barytes, and celestite, with which it would be expected to be isomorphous An important character is the cleavage in three directions parallel to the axial planes of symmetry; the mineral, therefore, breaks up into cubes like rock-salt. Well-formed crystals are not common; they have been found in the salt-deposits of Germany and Austria, and in dolomite-rock in the Simplon tunnel, in Switzerland. Usually, the mineral occurs as compact, granular masses of a white, grey, reddish, or bluish colour, and resembling marble in appearance. Sp.gr. 2·9–3·0; hardness 3–3½, being considerably higher than gypsum. It is of frequent occurrence as layers interbedded in deposits of gypsum and rock-salt. The 'anhydrite region' forming the base of the Prussian salt-deposits consists of alternating beds of anhydrite and rock-salt. Bands of anhydrite also occur throughout the salt-deposits, and are known to the miners as 'year-rings.' In contact with water anhydrite becomes altered into gypsum with an increase in volume of 60 p.c. On this account galleries in the salt-mines when driven through beds of anhydrite gradually become closed up. Extensive beds of the mineral occur in the gypsum deposits of Nova Scotia. In the red rocks of Permian and Triassic age of the North of England anhydrite is not uncommon. For example, it forms a bed 7 feet in thickness in the Cocklakes gypsum mine at Cumwhinton in Cumberland; and it is recorded from Durham, Westmoreland, Yorkshire, Staffordshire, Leicestershire, Nottinghamshire, Derbyshire, and Cheshire. For details of British occurrences, *see* Special Reports on the Mineral Resources of Great Britain, vol. iii, Gypsum and Anhydrite, Mem. Geol. Survey, London, 1915; 2nd edit., 1918.

Anhydrite has as yet been put to few practical uses. It has been employed in agriculture as a 'land plaster.' By exposure to the weather it becomes converted into gypsum, and can then be used for the manufacture of plasters. A bluish-violet, compact variety known as 'vulpinite,' from Vulpino in Lombardy, has been used as an ornamental stone. The suggestion to use gypsum as a source of sulphur would apply also to anhydrite. L. J. S.

ANIL. The name of the American species of the indigo plant, *Indigofera anil* (Linn.).

ANILINE.

History.—First observed by Unverdorben in 1826 among the products of the destructive distillation of indigo. Detected by Runge in coal tar in 1834, and by Fritzsche in 1840, among the products obtained by distilling indigo with alkali hydroxides. Prepared by Zinin in 1840, by the reduction of Mitscherlich's nitrobenzene with hydrogen sulphide. Unverdorben called his product *krystallin*; Runge, *kyanol*; Fritzsche, *anilin*; Zinin, *benzidam*.

In 1843 Hofmann showed that nitrobenzene could be reduced by a metal such as zinc in the presence of a dilute acid, and also that krystallin, kyanol, anilin, and benzidam were identical with each other. Shortly afterwards Bechamp stated that nitrobenzene could be reduced by ferrous acetate in the presence of water, but that the oxalate, sulphate, &c., had no effect.

In the year 1856 Perkin's discovery of mauve gave rise to a commercial demand for aniline, and the manufacture was commenced by Messrs. Simpson & Maule.

Preparation.—Benzene, then only obtained in small quantities and with much difficulty, as the treatment of tar scarcely existed, was introduced into glass balloons (known as 'bolt heads') of 1 gallon capacity, and the calculated quantity of nitric acid, mixed with about an equal volume of sulphuric acid, was gradually added, the mixture swung round and well agitated, and then allowed to stand. It was usual to have about twenty balloons in a row, and to add acid in turn until the reaction was complete.

The nitrobenzene was separated, washed, and reduced with iron borings and acetic acid, at first in a copper still, later in an iron cylinder. The aniline was freed from water, rectified, and was then ready for use. The selling price was about a guinea a pound.

Somewhat later cast-iron cylinders of considerable size were used for the reduction, acetic acid being still used and neutralised with soda or lime at the end of the reaction, and the aniline was in some factories distilled off over a naked fire, in others steam was blown into the mixture, and the aniline and water condensed and separated. Acetic acid continued to be used until about 1866. Since that time the apparatus has undergone little change, the treatment consisting in reduction mainly by the use of iron and water, hydrochloric acid being employed to start the reaction.

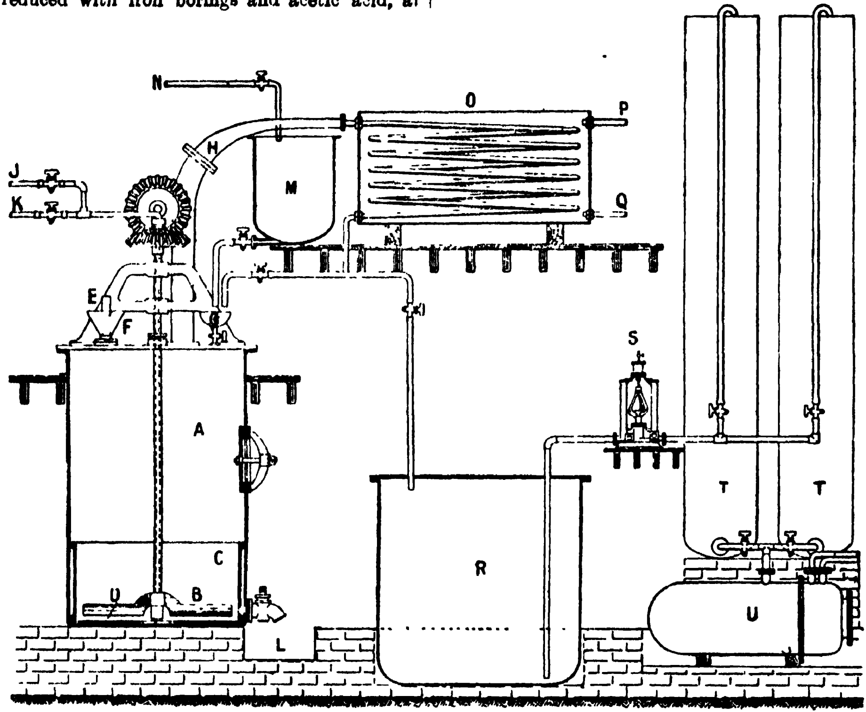

FIG. 1.—ANILINE OIL PLANT.

A, Aniline pan.
B, Agitating blades.
C, Side lining plates
D, Bottom do.
E, Wood plug for hopper

F, Feed hopper for borings.
G, Charging dish.
H, Vapour pipe to condenser
J, Pure-steam pipe.
K, Aniline-steam do.

L, Gutter.
M, Receiving pan.
N, Pipe from N B tank
O, Condenser
P, Overflow

Q, Cold-water inlet.
R, Receiver.
S, Steam pump.
T, Settling tubes
U, Air pressure egg.

The aniline machine shown in Fig. 1 is the type that gives the best results.[1] A careful comparison between this design and the horizontal machine has proved unmistakably that the vertical machine is more economical and better in every respect. This is particularly the case with regard to repairs and maintenance. The machine is of cast-iron, 1⅜ inches thick, with driving gear, agitating shaft, and blades, as shown in the sketch. An important feature is the renewable cast-iron lining plates at the sides and bottom, which protect the machine from the friction caused by the revolving mass of iron borings. It is 6 feet 6 inches deep, and 4 feet 6 inches in diameter, having a total capacity of 650 gallons. Steam is admitted through the vertical shaft, which is hollow, and passes through the extremities of the horizontal agitating blades. Twenty-one of these machines are required to produce 150 tons of aniline oil per month.[2] A charge of 1000 lbs. of nitrobenzene is run into the receiving pan above the machine.

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[1] See Chem. Trade J. 1906, 38, 59. The writer is indebted to Messrs Davis Bros. for permission to reproduce the two figures.

[2] Larger machines, on the same principle, in which several tons of nitrobenzene can be reduced, are used by some manufacturers.

To start the reaction, 1 cwt. of clean cast-iron borings, 10 gallons of hydrochloric acid, and 6 gallons of water are run in through the funnel-shaped hopper, and simultaneously steam is turned on and the nitrobenzene run in a thin stream into the dish on the top of the machine. The wooden plug in the hopper is driven in tight, and the space between it and the hopper is kept full of iron borings. By dexterously manipulating the wood plug, the borings can be added without allowing any vapour to escape. This simple method of 'feeding' the iron borings has proved better than many of the mechanical feeding devices that have been tried. Distillation proceeds, and the distillate passes through the condenser and runs back into the dish, together with the nitrobenzene which is carried over. The iron borings and nitrobenzene are added only in sufficient quantities to maintain a constant level in the dish. If the reaction proceeds too violently, loss is caused by the formation of benzene. When the level of the liquid in the dish begins to lower, the supply of nitrobenzene and iron borings is increased. This process is continued until the whole charge of nitrobenzene is run in, which takes about 10 hours. The total weight of iron borings required is 9 cwt. A sample caught as it runs from the condenser should then be quite free from nitrobenzene, and the machine will contain only aniline oil, water, and oxide of iron. The supply of steam is then increased, so as to distil over the aniline oil and water,[1] and the distillate is diverted into the tank beneath the condenser. The steam used for this distillation is not pure steam, but is generated from the aniline water mentioned below, in a separate boiler. The aniline water is that which separates from the oil in the separating tubes, and contains about 2 p.c. of aniline oil in solution. The aniline and water in the tank below the condenser are pumped into the settling tubes, and allowed to settle for 48 hours. The distillation of the oil and water from the machine takes about 7 hours, and during the last hour pure steam is again used, so that when the operation is finished, the condensed water left in the machine will be free from aniline, and can be used for flushing out the oxide of iron into the gutter which runs to the settling tanks outside. The oxide, after the water is drained off, is dried and ground, and disposed of for the purification of coal gas from sulphur. Large quantities are also now being used in the manufacture of cheap black paints, and the consumption in this direction is increasing. The aniline oil which has settled to the bottom of the settling tubes is run off into the air-pressure

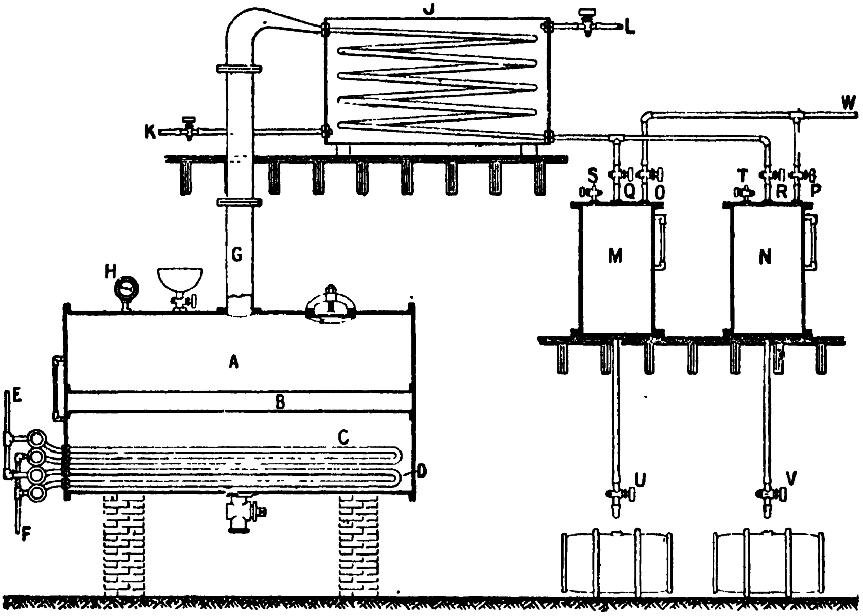

FIG. 2.—VACUUM STILL FOR ANILINE OIL.

A, Vacuum still.
B, Internal hollow stay.
C, Steam tubes.
D, Do. do.
E, Steam inlet.
F, Do. outlet.
G, Vapour pipe to condenser.
H, Pressure gauge.
J, Condenser
K, Cold-water inlet
L, Overflow for water
M, Receiver for distilled oil
N, Do. do. do
O, Connection from vacuum pump.
P, Do. do do.
Q, Inlet from condenser
R, Inlet from condenser.
S, Air-admission tap.
T, Do. do
U, Run-off tap for distilled oil.
V, Do. do. do.
W, Connection from vacuum pump

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[1] In some works this distillation is not done, but the contents of the reduction apparatus are passed immediately through a filter press, the filtrate then running directly or being pumped into the settling tanks.

egg below, and blown into the crude aniline oil store tanks, ready for the final purification by distillation in the vacuum still. The upper layer of water left in the settling tubes, and which contains about 2 p.c. of aniline in solution, is, as already explained, used for feeding the aniline steam boiler. The average yield of crude aniline oil from each machine, with a charge of 1000 lbs. of nitrobenzene, is 765 lbs. The yield of pure aniline oil from nitrobenzene is given further on.

The final purification of the crude aniline oil is done in a vacuum still. The sketch (Fig. 2) shows one of these stills of recent design. The body of the still is wrought-iron, 15 feet long, and 7 feet 6 inches in diameter, having a total capacity of 4000 gallons, and capable of distilling 35,000 lbs. in one charge. The steam is supplied from a boiler having a working pressure of 100 lbs. per sq. inch, at which pressure the steam possesses a temperature of 170°. The internal steam tubes are wrought-iron, 2 inches in diameter. In place of the usual straight tubes which used to be expanded into both end plates, bent tubes are employed, which enter and return to the same end of the still. This prevents the 'tearing' of the tubes owing to expansion and contraction, and the 'breathing' of the end plates. The 'column' is of cast iron, 18 feet high and 9 inches in diameter. The condensing coils consist of three vertical flat copper coils, 2 inches in diameter, arranged side by side in a wrought-iron tank, the distillate entering all the three coils simultaneously from the still head by means of branch pipes. The total length of copper pipe in the condenser is 432 feet. The two receivers permit continuous working, so that when the first is full, as indicated by the gauge-glass tube, it is shut off, and the second brought into use. The contents of the first can then be drawn off while the second is being filled, and the vacuum is thus maintained throughout.

The still is charged with 35,000 lbs. of crude aniline oil from the store tank, and steam is turned on. The first fraction, about 7 p.c. of the distillate, consists of aniline oil and water, which is added to the crude oil and water in the separating tubes. The next fraction is 'light aniline,' and consists of aniline oil with a small quantity of benzene. If the reduction of the nitrobenzene has been carefully performed, this fraction is only about 4 p.c. of the distillate. It is collected and redistilled, giving pure aniline and benzene, the latter being returned to the nitrobenzene department, to be renitrified. The next fraction is pure aniline oil of marketable quality, clear and water-white. The tail end, called 'last runnings,' forms about 5 p.c. of the distillate, and, on redistillation, yields 80 p.c. of pure marketable aniline oil. The total yield of pure aniline oil obtained from nitrobenzene is 71¾ p.c. As the pure benzene yields 154½ p.c. of nitrobenzene, and the latter 71¾ p.c. of pure aniline oil, the total yield of pure aniline oil from pure benzene is 110·85 p.c. Compared with theory, there is little room for improvement.

The process of reduction and rectification as described applies also to toluidine, and modifications of the process are also in use for the production of xylidine and alphanaphthylamine, and of the reduction portion for the manufacture of metaphenylene- and metatolylene-diamine from the respective dinitro- compounds.

Catalytic Reduction of Nitrobenzene.—This is effected by passing a mixture of nitrobenzene vapour and hydrogen (or other reducing gases) over a catalyst heated to a suitable temperature (usually 200°–300°). The catalysts which have been proposed are copper (Eng. Pats. 13149, 15334, 1914; 5692, 6409, 1915; U.S. Pat. 1207802; D. R. PP. 139457, 282568; Fr. Pat. 312615), nickel (Eng. Pats. 16936, 22523, 1913; D. R. P. 282492; Fr. Pats. 458033, and 1st addition), iron oxides (Fr. Pat. 462006), iron (D. R. P. 281100), and silver or gold (D. R. P. 263396).

Many patents have been taken out for the electrolytic reduction of nitrobenzene, but it is doubtful whether this process is used on the large scale.

The reduction of nitrobenzene may also be carried out by boiling it with sodium disulphide solution (D. R. P. 144809), and an 80 p.c. yield of aniline is said to be obtained by heating chlorobenzene with ammonia and a little copper sulphate (Eng. Pat. 3966, 1908; D. R. P. 204951; Fr. Pat. 397485).

Valuation of Commercial Aniline Oil.

Aniline oil, as it occurs in commerce, may contain as impurities water, traces of insoluble hydrocarbons and of orthotoluidine, sometimes traces of hydrogen sulphide, and, if carelessly made, of nitrobenzene, benzene, and ammonia. Besides these, which should be carefully tested for, there is possibly a certain amount of aminothiophen, which has no deleterious action for most, if not all, of the purposes for which aniline is used, and which, moreover, for the present at least, cannot readily be got rid of.

The method of testing usually adopted is to determine the boiling-point of the sample. For this purpose 100 c.c. are introduced into a small boiling flask with side tube, and distilled through a short condenser into a graduated 100 c.c. cylinder. Readings of the thermometer are taken as each 10 c.c. of the cylinder fills, and the last when 95 c.c. are filled. An alternative method is to take readings of the cylinder at each fifth of a degree rise of the thermometer. It is also usual to note the temperature when the first drop has fallen from the condenser. The thermometer readings should be corrected for barometer and immersion of mercurial column in the vapour of the liquid, and of course for the errors peculiar to the thermometer in use.

A few fragments of platinum wire, fire-brick, or wrought iron, should be placed on the bottom of the flask, and great care used to adjust the size of the flame and rate of boiling. The flask also should be held by the neck in a good clip over the naked flame, gauze being apt to cause currents of heated gas to flow up round the neck of the flask and superheat the vapour.

The specific gravity of the sample may also be taken (pure aniline has a specific gravity of 1·0265–1·0267 at 15°), although this indication is not of great moment if the boiling-points are good.

The following is an example of the determination of the boiling-point (Walter, Chem. Zeit. 1910, 34, 702):—

Temperature.	P.c. over.	Temperature.	P.c. over.
182·4°	3	183·2°	20
182·6°	4	183·4°	97
182·8°	5·5	183·6°	98
183·0°	11	183·8°	99

If, in carrying out the boiling test, the temperature rises considerably at the end, the presence of toluidine may be suspected. This can be detected when a considerable quantity of commercial pure aniline is made into acetanilide. On recrystallising this and working up the mother liquors, a small quantity of impure acetyl compound of low melting-point will always be found in the most soluble portion, or first mother liquors.

Pure aniline melts at −6·2°, and boils at 80°–81°/20 mm. and 184·4°/760 mm.

Aniline may be tested for insoluble oils by dissolving 10 c.c. in 40 c.c. of hydrochloric acid and 50 c.c. of water. The solution should be quite clear.

Nitrobenzene shows itself with the insoluble hydrocarbons. A very delicate test for it is to shake the sample of aniline violently for a few minutes, and then to notice the colour of the froth. The merest trace of nitrobenzene colours it a very distinct yellow.

The presence of water may be detected by distilling the sample (100 c.c.) as for a boiling-point determination, and collecting the first 10 c.c. in a narrow graduated cylinder of 15 c.c. capacity, shaking with 1 c.c. of saturated sodium chloride solution, and reading off the volume of the latter. The method will not show the presence of less than 0·3 p.c. of water, consequently, 0·3 c.c. must always be added to the amount of salt solution observed. It is not usual for aniline, sold as pure, to contain more than 0·5 p.c. of water.

Toluidine liquid should boil at 197°–198°, show a sp.gr. of about 1·000, and contain 30–40 p.c. para-, the rest ortho- toluidine.

Orthotoluidine. The sp.gr. of commercial orthotoluidine should be about 1·0037; b.p. about 197°–198°; should not solidify on cooling to −4°. The pure substance boils at 199·7°, and does not solidify at −20°. Its density at 15°, compared with water at 15°, is 1·0031.

Paratoluidine. When pure, this melts at 45° and boils at 200·4°/760 mm. and 86°–87°/10 mm. Its density is 1·046. Lunge (Chem. Ind. 1885, 8, 74) has published a table showing the specific gravities of mixtures of *o*- and *p*-toluidine.

For the estimation of small amounts of *p*-toluidine in *o*-toluidine, Schoen's method is perhaps the best. A standard oil is prepared, containing 8 p.c. of *p*-toluidine and 92 p.c. of *o*-toluidine, 1 c.c. of which is dissolved with 2 c.c. of pure hydrochloric acid in 50 c.c. of water, and oxidised cold by adding 1 c.c. of a saturated solution of potassium dichromate. After standing for two hours, the product is filtered, the precipitate being washed with water, and the filtrate and washings made up to 100 c.c. The toluidine to be tested is treated in the same manner, and compared colorimetrically with the above solution. J. C. C.

ANILINE BLACK *v.* Dyeing.

ANILINE BLUE *v.* Triphenylmethane colouring matters.

ANILINE BROWN *v.* Azo- colouring matters.

ANILINE SALT. The commercial name of aniline hydrochloride $C_6H_5{\cdot}NH_2,HCl$.

It is prepared in large quantities, for the use of calico-printers, who employ it in the production of aniline black. The process consists in mixing the calculated quantities of pure aniline and hydrochloric acid in lead-lined or nickel-lined tanks, and allowing the salt to crystallise, freeing it from mother liquors in a centrifugal machine, and drying at a low temperature. The hydrochloric acid used should be of good quality, free from iron and even from traces of copper, or the salt will rapidly blacken.

The mother liquors may be neutralised with lime or soda, and the aniline recovered, or they may be boiled down and used in making magenta by the nitrobenzene process, &c.

'Aniline salt' occurs in commerce in large white, nacreous and much-contorted plates.

The great desiderata for the calico-printer are that the salt should be made from pure aniline and should be dry and normal, containing 93 parts of aniline to 36·5 parts of hydrochloric acid; it should be free from sand and grit, which injure the printing machines.

J. C. C.

ANILINE YELLOW *v.* Azo- colouring matters.

ANIMAL OILS and **FATS** *v.* Oils and fats.

ANIME and **ANIMI** *v.* Oleo-resins.

ANISEED. (*Anis*, Fr., Ger.) The fruit of the *Pimpinella Anisum* (Linn.), cultivated in Malta, Spain, and Germany. Used for the preparation of anise oil and cordials. Alcohol extracts 36·24 p.c. of this spice (Biechele, Pharm. J. [3] 10, 878).

ANISE CAMPHOR *v.* Camphors.

ANISE OIL. The essential oil of aniseed, obtained by distilling it with water. According to Landolph (Compt. rend. 81, 97; 82, 226), it contains 90 p.c. of *anethole*, boiling at 22·6°. Anethole, according to Perkin (Chem. Soc. Trans. 32, 668), is p-allylanisole $C_6H_4(OMe)CH:CH{\cdot}CH_3$; he obtained it by heating p-methoxyphenylcrotonic acid.

Anise oil is sometimes adulterated with fennel oil; this can be detected by heating the oil, when the fennel odour becomes perceptible.

Star anise oil has a similar colour and taste, but it does not solidify at 2° (*v.* Oils, Essential).

ANISIDINE. $NH_2{\cdot}C_6H_4{\cdot}OMe$. *Orthanisidine.* Obtained by the reduction of orthonitranisole with tin and hydrochloric acid or iron and hydrochloric acid (Meister, Lucius, and Brüning, D. R. P. 7217 of Dec. 3, 1878), is a colourless oil, which freezes at 2·5°, boils at 226·5° at 734 mm. pressure (Mülhaüser, Annalen, 207, 239); at 225° at 760 mm. (Perkin, Chem. Soc. Trans. 69, 1210), and has a sp.gr. 1·108 at 26°. Can also be prepared by heating a mixture of *o*-aminophenol, potassium methyl sulphate, and potassium hydroxide solution under pressure. When diazotised and treated with β-naphtholdisulphonic acid (R-acid), it yields *anisole-red* (*v.* Azo- colouring matters). A mixture of orthanisidine (2 mols.) and paraphenylenediamine (1 mol.) is converted, on oxidation with potassium dichromate, into a reddish colouring matter formerly employed under the name *safranisole* (Kalle & Co., D. R. P. 24229 of Oct. 27, 1882; expired March, 1885). Anisidine is used for making chrome fast yellow G-G. azoeosin G and azocochineal.

Paranisidine, obtained from paranitranisole by reduction with tin and hydrochloric acid, crystallises in prisms which melt at 55·5°–56·5° (Lossen, Annalen, 175, 324) and boil at 245°-246° (Salkowski, Ber. 7, 1009); 243° at 760 mm. (Perkin, Chem. Soc. Trans. 69, 1210); *p*-anisidine, *o*-sulphonic acid, prepared by boiling the hydrogen sulphate of *p*-anisidine, when diazotised and coupled with *β*-naphthol, yields an azo-compound forming red lakes with baryta, alumina, &c. (Aktiengesellschaft fur Anilin-Fabrikation, D. R. P. 14665).

Chloranisidine, when diazotised and coupled with *β*-naphthol, yields a red compound insoluble in water (Julius, Ludwigshafen and Jahrmaht, U.S. Pat. 695812); *p*- and *m*-nitroanisidine, when diazotised and coupled with *β*-naphthol, yield red and pink dyestuffs (Imray, Eng. Pat. 25756; J. Soc. Chem. Ind. 1898, 1039; and Freyss, J. Soc. Chem. Ind. 1901, 356); *o*-iodo-*p*-anisidine, when diazotised and treated with naphthol sulphonic acid, yields a red dye, similar to that obtained from *p*-anisidine (Reverdin, Ber. 29, 997).

Anisidine condenses with orthoformic ester, and the resulting compound is used as an anæsthetic (Goldchsmidt, Eng. Pat. 9792; J. Soc. Chem. Ind. 1899, 606).

ANISOCHILUS CARNOSUS (Wall.). An Indian plant belonging to the Labiatæ and containing a volatile oil. Used in quinsy.

ANISOLE. *Anisoil; Methylphenyl ether*

$C_6H_5{\cdot}O{\cdot}CH_3$.

Preparation.—Anisole can be obtained by distilling anisic acid or *o*-methoxybenzoic acid with baryta, or by heating potassium phenate with methyl iodide at 120° (Cahours, Ann. Chim. Phys. [3] 2, 274; 10, 353; 27, 439). It is prepared by passing a current of methyl chloride over dry sodium phenate heated at 190°-200° (Vincent, Bull. Soc. chim. 40, 106), and by heating phenol with methyl alcohol and potassium bisulphate at 150°-160° (Act. Ges. für Anil.-Fabrik.; D. R. P. 23775). It has been synthesised by fusing sodium benzene sulphonate with sodium methoxide (Moureu, J. Pharm. Chim. 8, v. 211).

Properties.—It is a colourless ethereal liquid, which boils at 155°-155·5° at 762·3 mm. (Schiff, Annalen, 220, 105) at 153·9° (corr.) (Perkin, Chem. Soc. Trans. 69, 1240); melts at −37·8° (Von Schneider, Zeit. Phys. Chem. 19, 997) and has a specific gravity 0 991 at 15° (*v.* OILS, ESSENTIAL).

ANISOMELES MALABARICA (R. Br.). A much-esteemed Indian plant belonging to the Labiatæ; an infusion of the leaves is used in intermittent fevers, and the essential oil is applied externally in rheumatism.

ANISOTHEOBROMINE. Trade name for an addition product of theobromine sodium and sodium anisate.

ANKERITE. A member of the group of rhombohedral carbonates containing calcium, magnesium, and iron, with sometimes a little manganese. The formula is like that of dolomite with the magnesium partly replaced by iron; in normal ankerite it is $CaCO_3{\cdot}Mg_{\frac{1}{2}}Fe_{\frac{1}{2}}CO_3$. The angle between adjacent faces of the rhombohedral cleavage is 73° 48′. D 2·95–3·1; H 3½–4. The mineral forms white, greyish, or brownish cleavage rhombs, cleavage masses, or granular masses. It occurs in some abundance with chalybite ($FeCO_3$) in the iron mines of Eisenerz in Styria, Londonderry in Nova Scotia, and in northern New York. The white, thin platy seams often seen in coal consist usually of ankerite. L. J. S.

ANKOOL, AKOLA, DHERA, BARK. The root bark of *Alangium Lamarckii* (Thw.), one of the Cornaceæ, used in leprosy and skin-diseases (Dymock, Pharm. J. [3] 9, 1017).

ANNATTO. This is derived from the fruit of the *Bixa orellana* (Linn.), a shrub found native in Central America, and cultivated in Brazil, Guiana, Mexico, the Antilles, and India.

To prepare the dyestuff, the seeds and pulp are removed from the mature fruit, macerated with water, and the mixture is left to ferment. The product is strained through a sieve, and the colouring matter which settles out is collected, partially evaporated by heat, then placed in boxes, and finally dried in the sun.

Annatto comes into the market in the form of cakes, and among the different varieties Cayenne annatto is the most esteemed, and is considered to be the richest in colouring matter. It should contain from 10 to 12 p.c. of the pure dye, and not more than 5 p.c. of ash, whereas the amount of colouring matter in the Bengal product is frequently lower than 6 p.c.

In 1848 Dumontal devised a new method for the preparation of annatto, in which fermentation is avoided, and the pulp is simply washed out from the capsules and off the seeds. This product known as *bixin* is said to be five to six times more valuable than ordinary annatto (Crookes, Dyeing and Calico-Printing).

The colouring matters of this dyestuff were first investigated by Chevreul (Leçons de Chimie appliquée à la Teinture), who isolated two substances, one yellow, which was called *orrellin*, soluble in water, and a second, *bixin*, which is red and very sparingly soluble.

Bixin, the useful colouring matter, was subsequently examined by numerous chemists, who were only successful in preparing it as an amorphous powder, and its isolation in a crystalline condition was first achieved by Etti (Ber. 7, 446; 11, 864).

Etti digested 1·5 kilos of purified annatto with a solution of 150 grams of calcined soda ash in 2·5 kilos of 80 p.c. alcohol on the water-bath at 80°. The mixture was filtered and the residue pressed between warm plates, and again extracted with 1·5 kilos of warm 60 p.c. alcohol.

The alcoholic filtrate was diluted with half its volume of water, concentrated, sodium carbonate solution added, and the crystalline precipitate of sodium bixin was collected after several days, and pressed. The product purified by solution in 60 p.c. alcohol at 70°–80° and reprecipitation with sodium carbonate was finally made into a cream with alcohol, and this, when neutralised with hydrochloric acid, yielded crystalline bixin.

A simpler method has been more recently devised by Zwick (Ber. 30, 1972). Well-dried annatto is extracted for twenty-four hours with boiling chloroform, the extract evaporated, and the residue thoroughly exhausted with ligroin. The product is crystallised from chloroform, and after washing with ligroin is repeatedly recrystallised from the former solvent.

Bixin $C_{28}H_{34}O_5$ (Etti, *l.c.*; Marchlewski and Matejko, Chem. Zentr. 1906 [ii.] 1265) consists of brown-red or deep-red rhombic crystals, which, when slowly heated, melt at 191·5°, and when rapidly heated at 198°. It is sparingly soluble in the usual solvents, and of these it is most readily dissolved by chloroform or alcohol. Concentrated sulphuric acid dissolves bixin with a cornflower-blue colouration, and this reaction is given by minute traces of the substance (*cf.* Crocin and Nycanthin).

Monosodium bixin $C_{28}H_{33}O_5Na+2H_2O$ is best prepared by dissolving 10 grams of bixin in a solution of 1·2 grams of sodium carbonate in 300 c.c. of 12 p.c. alcohol at 70° (Etti, Zwick). It is deposited on cooling in dark-red iridescent crystals, and can be obtained in the anhydrous condition by recrystallisation from 70 p.c. alcohol (Marchlewski and Matejko).

Disodium bixin $C_{28}H_{32}O_5Na_2+2H_2O$ is obtained when 20 grams of bixin is dissolved in a solution of 10 grams sodium carbonate in 600 c.c. of boiling 12 p.c. alcohol. It consists of a dark-red amorphous powder (Etti). *Monopotassium bixin* $C_{28}H_{33}O_5K+H2_2O$ and *dipotassium bixin* $C_{28}H_{32}O_5K_2+2H_2O$ have also been prepared.

Bixin contains one methoxyl group. Distilled with zinc-dust, bixin yields, according to Etti, *metaxylene*, *metaethylxylene*, and a hydrocarbon $C_{14}H_{14}$, b.p. 270°–280°.

According to Zwick, bixin is readily reduced by sodium amalgam, and a compound $C_{23}H_{40}O_7$ is thus produced. Marchlewski and Matejko, on the other hand, studied the action of zinc-dust and acetic acid, and obtained in this manner an orange-coloured crystalline substance which possessed a strong metallic lustre. When slowly heated it melts at 200·5°, but if the operation is carried out rapidly, at 208°–210°. This compound is evidently of an unstable nature, for whereas when freshly prepared it gives C=75·4, H=7·7 p.c., on standing for some days in the air it becomes colourless and then gives C=58·6, H=5·8 p.c. At 100° this change occurs more rapidly.

More recently there has been much controversy as to the correct formula for bixin.

Van Hasselt (Chem. Weekblad, 1909, 6, 480) contends that pure bixin, which melts at 189°, is $C_{29}H_{34}O_5$ rather than $C_{28}H_{34}O_5$, as proposed by Etti (*l.c.*). If heated at 190° in a current of hydrogen, 1 gram mol. of bixin yields 1 gram mol. of *m*-xylene, and no other volatile product, though it is not to be considered that a *m*-xylene nucleus exists as such in the bixin molecule. No palmitic acid could be obtained from bixin as Zwick suggests. Whereas both Etti and Zwick described mono- and dipotassium salts of bixin, the latter is not in reality a compound of bixin, but of a new substance termed *norbixin* $OK·C_{28}H_{30}O_3·OK$, produced by a substitution of a methyl of the methoxy group present in the former by potassium (Rec. trav. chim. 1911, 30, 1). Norbixin $C_{28}H_{32}O_5$ consists of a light red-coloured crystalline powder which decomposes at about 240°, and is distinguished from bixin by its insolubility in chloroform.

Potassium bixinate with methyl sulphate gives *bixin methyl ether* $B(OMe)_2$, or $C_{30}H_{36}O_5$, plates, m.p. 156° (1909), and the same compound is obtained when a solution of bixin in methyl alcohol is treated with potassium hydroxide and methyl sulphate (1911). On treatment with potassium hydroxide, bixin methyl ether is converted into norbixin. *Bixin ethyl ether* $C_{31}H_{38}O_5$, violet crystals, melts at 138°, and by methylation forms *norbixin methyl ethyl ether* OMe·B·OEt, m.p. 149°.

Potassium norbixin, obtained from bixin and alcoholic potash, gives with ethyl sulphate *norbixin diethyl ether* $C_{28}H_{30}O_3(OEt)_2$, m.p. 121°, together with *norbixin ethyl ether*

$$C_{28}H_{30}O_3(OEt)(OH),$$

m.p. 176°.

The relationship between norbixin, bixin, and bixin methyl ether is shown as follows :—

OH·R·OH OH·R·OMe OMe·R·OMe

According to Hasselt, *iso-bixin methyl ether*, m.p. 149°, is produced when norbixin ethyl ether is methylated, and it is thus evident that the two hydroxyls of norbixin are not symmetrically situated. *Iso-bixin* OH·R·OMe, melts at 178°, and may be obtained by the partial hydrolysis of bixin methyl ether, and this, by ethylation with ethyl sulphate, gives norbixin diethyl ether, m.p. 121°, the methyl being thus replaced by an ethyl group. Iso-bixin is distinguished from bixin by the greater stability of its methyl group in presence of potassium hydroxide solution.

The product of the reduction of bixin obtained by Marchlewski and Matejko, and referred to above, is considered by van Hasselt to consist of *dihydrobixin* $C_{29}H_{36}O_5$. He has also described *dihydrobixin methyl ether* $C_{30}H_{38}O_5$, m.p. 174°; *dihydro-iso-bixin* $C_{29}H_{36}O_5$, m.p. 190°; and *dihydro-norbixin* $C_{28}H_{34}O_5$, which decomposes at 235°.

By the action of bromine, bixin yields *bixin decabromide* $C_{29}H_{34}O_5Br_{10}$, whereas bixin methyl ether yields the analogous compound

$$C_{30}H_{36}O_5Br_{10},$$

and both these substances are colourless amorphous powders. Attempts to benzoylate or acetylate bixin were unsuccessful.

On the other hand, Heiduschka and Riffart (Arch. Pharm. 1911, 240, 43) consider that the old formula $C_{28}H_{34}O_5$ for bixin is preferable to that of $C_{29}H_{34}O_5$, advocated by van Hasselt. Bixin, by the action of bromine in the presence of chloroform, gives the compound $C_{28}H_{34}O_5Br_{10}$, 4HBr, melting at 143°, and this by heating at 100° is converted into the decabromide $C_{28}H_{34}O_5Br_{10}$, which can be obtained crystalline from alcohol, but is unstable. By the action of chlorine on bixin and norbixin respectively, the amorphous compounds $C_{28}H_{34}O_5Cl_{10}$, 4HCl and $C_{27}H_{32}O_5Cl_{10}$, 4HCl can be prepared.

Van Hasselt (Rec. trav. chim. 1914, 33, 192), however, maintains that his formula for bixin $C_{29}H_{34}O_5$ is correct, and states that the discrepancy shown by the results of his own work and that of Heiduschka and Riffart arises from the fact that bixin is readily susceptible to oxidation with the formation of amorphous products. The bixin of these latter authors was not completely pure, and it is quite correct that specimens which are purified by their method give figures in harmony with the older formula $C_{28}H_{34}O_5$. Again, the analytical numbers given by Marchlewski and Matejko for hydrobixin are explainable if bixin is given the formula $C_{29}H_{34}O_5$.

A new formula $C_{25}H_{27}O_3 \cdot OMe$ for bixin was now suggested by Herzig, Faltis, and Mizzan (Monatsh. 1914, 35, 997), who state that it is difficult to correctly analyse bixin unless special precautions are adopted. *Dihydrobixin*, the product of the action of zinc-dust and acetic acid on bixin, melts at 178°–179°, whereas the methyl ether obtained by means of diazomethane and bixin, or methyl sulphate and potassium bixin, melts at 158°.

Though, as Hasselt states, bixin at 190°–200° yields *m*-xylene, the reaction is hardly of a quantitative nature, in that the crude oil, though containing this hydrocarbon, possesses no constant boiling-point. Rinkes (Chem. Weekblad) suggests that the formula of bixin is $C_{27}H_{32}O_4$, though Herzig and Faltis (Ber. 1917, 50, 927) in reply, reiterate that the expression $C_{26}H_{30}O_4$ is to be regarded as correct, and that the real difficulty lies in the combustion of this colouring matter. Heiduschka and Panzer (Ber. 1917, 50, 546) point out, however, as the result of further investigation, that the main difficulty is in the purification of the substance. The most satisfactory products are those obtained by means of acetone and ethyl acetate, which, when analysed, give figures agreeing with the formula $C_{25}H_{30}O_4$.

When ozonised, methyl bixin forms an *ozonide*, and this by distillation, and partly by the action of calcium carbonate, gives among other products, *methyl-β-acetyl acrylate*, and a crystalline compound $C_8H_{10}O_3$, m.p. 85°, which yields an oxime, m.p. 106°, and may be the methyl ester of a ketonic acid. Methylbixin thus appears to contain the linkage

$$\ddot{C}\cdot Me\cdot CH : CH\cdot \ddot{C}\cdot OMe$$

(Rinkes and Hasslet, Chem. Weekblad, 1916, 13, 244, and 14, 888).

Sodium hyposulphite reduces bixin to *α-hydrobixin*, red needles, melting about 200°, norbixin to *α-hydronorbixin*, violet crystals, and methylbixin to *α-hydromethylbixin*, violet needles, m.p. 190°–192°.

On the other hand, with titanium sesquioxide, bixin gives *β-hydrobixin*, norbixin *β-hydronorbixin*, and methylbixin *β-hydromethylbixin*, the latter of which melts at 170°. By the action of zinc-dust both *α*- and *β*-hydrobixins are converted into the same *γ-hydrobixin*, yellow crystals, m.p. 207° (van Hasselt, *ibid.* 1916, 13, 429).

In a further communication Heiduschka and Panzer (Ber. 1917, 50, 1525) again maintain the probability of the formula $C_{26}H_{30}O_4$ for bixin.

Dyeing Properties.—Annatto is still employed to a fair extent for colouring oils and butter, but is almost extinct as a dyestuff in this country. As the orange-red colour which it yields is extremely fugitive to light, it has at no time been very extensively used. On the other hand, it resists the action of soap and dilute acids very well.

In order to dye cotton, the annatto is first dissolved in a boiling solution of carbonate of soda, and the goods are then entered and left in the bath for a quarter of an hour. They are subsequently pressed out, and washed in slightly acidulated water or alum solution.

For silk, the bath is made up with equal parts of annatto and sodium carbonate; soap is also usually added, and the dyeing is continued at 50° for about an hour, according to the shade required. The colour produced can be rendered somewhat more yellow by passing the fabric through a weak solution of tartaric acid.

Wool is dyed at 80°–100° without any addition to the bath. A. G. P.

ANNEALING. (*Le recuit*, Fr.; *das Anlassen*, Ger.) A process which is applied principally to glass and metals for the purpose of rendering them softer or less brittle. The process itself always consists in the application of heat for a period of time, which may vary from a few minutes to many hours, and which may be followed by very slow cooling; the object of the process is to permit the material to attain approximate equilibrium in regard to its internal structure. This state of normal internal equilibrium may be disturbed either by the effects of rapid cooling or by the application of mechanical deformation. The former is most frequently met with in glass, and in large metal castings, while the latter is found in 'wrought' metal of all kinds.

In the case of substances which are poor conductors of heat, such as glass, and also in masses of metal which are so large that thermal conductivity cannot produce reasonable uniformity of temperature, relatively rapid cooling sets up severe stresses, owing to the fact that the outer or most rapidly cooled layers solidify or become hard and rigid first; subsequently the internal portions of the mass endeavour to contract in cooling, but find themselves constrained by their attachment to a relatively rigid external envelope; the tendency to thermal contraction is therefore overcome by severe tensional stresses. A body in this condition, while it may present the phenomenal strength of a 'Rupert's drop,' is liable to sudden fracture, particularly if the surface is cut or broken. The annealing of glass has been studied with great care (Twyman, Journ. Soc. Glass Technology, vol. i. 1, pp. 61–74), and it has been shown that glass behaves as a true fluid whose change of viscosity with temperature follows an exponential law, so that the viscosity is halved for each rise of temperature of 8° C. If, then, a piece of glass has been so cooled as to be heavily stressed internally, these stresses will be released if the temperature is raised to such a point that the viscosity becomes low enough for appreciable flow to take place in a few seconds. The temperature required for this purpose may be defined as 'the annealing temperature,' and although it is not a definite critical temperature, the rapidity with which the viscosity or 'stiffness' of the glass changes with temperature makes it possible to approximate to a definite 'annealing temperature' for each kind of glass. Experimentally this may be done by heating an internally-strained specimen of the glass in an electric tube-furance while keeping it under observation by means of a beam of plane-polarised light passing through the glass while in the furnace-tube. When thus examined under 'crossed Nicols' the presence of internal stress makes itself apparent by a more or less well-defined cross, or at least by light and dark shading. This appearance remains practically unchanged (unless the heating is very slow), until the annealing temperature is reached, when the markings suddenly disappear. Such glass can then be fully annealed by heating to this temperature, followed by cooling in such a manner that no fresh internal stresses are set up. This usually implies very slow cooling until the glass is stiff enough to be free from further risk in this respect. It should be noted, however, that slow cooling in itself is of no special advantage; all that is required is the maintenance of the greatest possible uniformity of temperature throughout the mass so that all parts of it shall cool as nearly as may be simultaneously. In bodies like glass, which are poor conductors of heat, this can only be attained by extremely slow cooling, except where very thin pieces are concerned. In the case of metals, which are good conductors of heat, extremely slow cooling is not necessary in order to avoid the development of severe internal stresses, and as very slow cooling is undesirable in most metals because of the tendency to produce coarse and weak microstructures, it is never employed intentionally. Annealing is, in fact, generally applied to metals for other purposes.

Metals in the cast or other 'normal' condition consist of aggregates of minute crystals of approximately equal dimensions in all directions; when metal is mechanically deformed, as by hammering, rolling, or other working process carried on in the cold, these minute crystals are elongated in the same general sense as the mass of which they form part, and this deformation of the crystals is accompanied by the well-known hardening of the metal under cold work. This is due in part to the internal rearrangement which each crystal undergoes, and in part to the partial and local destruction of the crystalline arrangement itself, accompanied by the formation of a hard amorphous 'phase' (Ewing and Rosenhain, Phil. Trans. 1899, ser. A. cxcii. 353–375; Beilby, Phil. Mag. 1894). When the metal is subsequently annealed, *i.e.* heated to a suitable temperature, the metal 'recrystallises,' the crystals rearrange themselves, and the original condition is approximately restored. In some metals the molecular mobility is such that recrystallisation takes place slowly even at the ordinary temperature (lead: Ewing and Rosenhain, Phil. Trans. 1900, cxcv. 279–301; brass: Cohen, Rev. general des Sciences, April 30, 1910); but in the greater number of cases a high temperature is required. In the great majority of pure metals, and in some alloys, the rate of subsequent cooling is immaterial so far as the softening effect is concerned; but in certain metals and in a large number of alloys either allotropic or other changes take place during gradual cooling, and these transformations are more or less inhibited by rapid cooling; in such metals the rate of cooling through the 'critical temperatures' at which these changes occur is of material importance. The most striking example is found in carbon steels containing upwards of ½ p.c. of carbon, which are moderately soft if cooled slowly down to a temperature of 650°, but become exceedingly hard if suddenly cooled from a temperature above 700°. In the case of hardened tool steel, the process of annealing consists in raising the steel to such a temperature (above 700°) that the changes which were suppressed when the steel was hardened by quenching are allowed to take place during the heating and cooling process.

In modern 'high speed tool steels' the presence of a considerable percentage of tungsten (16–20 p.c.) or of molybdenum, has the effect of raising the annealing or softening temperature very considerably. Prolonged exposure to a temperature near 900° C. is required to bring about full softening, and tools made of these steels retain their cutting edge at a dull red heat (near 700° C.), while a carbon steel becomes useless at a much lower temperature (near 400° C.). It is this property which makes it possible to use 'high speed' tools for working at rates which generate far more heat than carbon steel tools could withstand.

A special form of annealing known as 'normalising' is now frequently applied to mild steel with highly beneficial results. The process consists in heating the steel to a temperature just above the highest critical point (from 830° C. to 900° C., according to the carbon content), keeping it there just long enough to ensure that the whole mass has attained the desired temperature, and then allowing the steel to cool rapidly, usually by taking it out of the furnace and cooling it in the air. This treatment results in the refining of the structure of the steel (*see* METALLOGRAPHY) with a very considerable concomitant improvement in the physical properties, more especially as shown by the notched-bar impact test.

In many metals the annealing process is liable to be complicated by the effects of chemical actions between the metal and its solid or gaseous surroundings, as well as by the effects of the growth of the constituent crystals of the metal; at high temperatures these crystals tend to increase in size, and the resulting coarsening of the grain of the metal leads to a deterioration in mechanical properties. Annealing at an unduly high temperature or for too long a time thus becomes 'over-heating,' and is injurious to almost all metals and alloys, notably to steel and brass. W. R.

ANODYNINE. Identical with antipyrine (*q.v.*).

ANOGON. Trade name for the mercury salt of 2·6-diiodophenol-4-sulphonic acid.

ANONA MURICATA (Linn.). A decoction of the root is used as an antidote for fish-poisoning, and the bark serves as an astringent. The leaves are useful in softening abscesses, and from the seeds a wine can be prepared which is said to be beneficial in cases of diarrhœa (Chem. Zeit. 10, 433; J. Soc. Chem. Ind. 5, 332).

ANORTHITE *v.* FELSPAR.

ANOZOL. Trade name for a preparation of iodoform deodorised by 10–20 p.c. of thymol.

ANTACEDIN. *Calcium saccharate.*

ANTALGINE. Trade name for salicylaldehyde-α-methylphenyl hydrazone. Used for neuralgia and rheumatism.

ANTHEMOL *v.* CAMPHORS.

ANTHIONE. Trade name for a solution of potassium persulphate. Employed as a photographic reagent.

ANTHOCYANINS. Many brilliant natural effects are due to the colouring matters of this group. They have been the subject of investigation for many years past, but it is only since the work of Willstatter and Everest (Annalen, 1913, 401, 189) that chemical knowledge concerning them has been placed upon a satisfactory basis.

Marquart (Die Farben der Blüten, Bonn, 1835) first introduced the term *anthocyan*, using it for the blue pigments present in flowers; gradually, however, the term became extended to include all red, purple, and blue flower, berry, or leaf sap-pigments, whilst the terms *anthocyanin* and *anthocyanidin* were introduced by Willstatter and Everest to designate the glucoside and non-glucoside anthocyan pigments respectively.

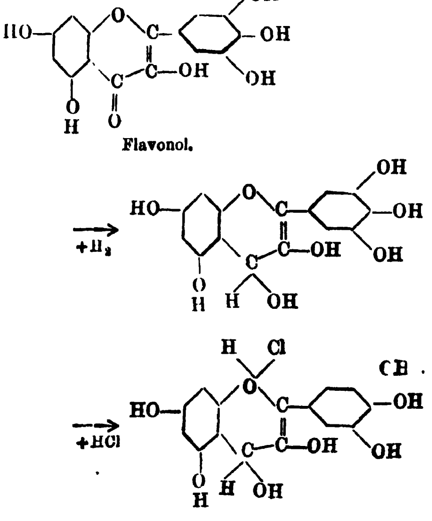
In 1837, Berzelius (Annalen, 21, 262) attempted to isolate and purify various pigments of this class, and his method, which involved the use of lead salts, was adopted by many later investigators, but rarely with any success. Morot (Annales des Science nat. [3] 13, 160 [1849-1850]) attempted to obtain a pure pigment from the cornflower, whilst Fremy and Cloëz (J. Pharm. Chim. [3] 25, 249) worked on various flowers, including the cornflower, violet, iris, dahlia, rose, and peony, and concluded that all anthocyan colours were produced by a single pigment which they called *Cyanin*. (This name was given to the cornflower pigment in 1913 by Willstatter and Everest.) In connection with the supposed identity of all anthocyan pigments the work of Overton (Pring. Jahrber. f. wiss. Bot. 1899, 33, 222), of Weigert (Jahresber. d. k. k. önol. und pomol. Lehranstalt in Klosterneuburg, 1894-1895), and the earlier work of Berzelius (*l.c.*), Fremy and Cloëz (*l.c.*), Filhol (Compt. rend. 39, 194; J. pr. Chem. 1854, 63, 78), Wigand (Bot. Ztg. 1862, 123), Hausen (Die Farbstoffe der Blüten und Früchten, Würzburg, 1884, 8), and Wiesner (Bot. Ztg. 1862, 392), should be referred to.

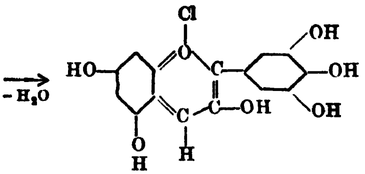
Filhol (*l.c.* 1854) and Morren (1859) carried out a number of qualitative investigations bearing upon the formation of pigments in flowers.

Work of a more definitely quantitative character was attempted by Glénard (Compt. rend. 47, 268; Jahrber. 1858, 476), using red wine, and Senier (Jahrber. 1878, 970), using *rosa gallica*, and this was followed by that of Heise (*cf.* Chem. Centrblt. 1889, ii. 953; and 1894, ii. 846) and Glan (Dissertation, Erlangen, 1892), in which the pigments of red wine, the bilberry, and flowers of the deep-red hollyhock were examined, and as the result of this the question of the glucosidal nature of these pigments was raised, a question first settled by the work of Willstatter and Everest in 1913.

The first description of an anthocyan pigment in crystalline condition was published by Griffiths (Ber. 36, 3959; Chem. News, 1903, 88, 249), the pigment being that of the scarlet pelargonium. Somewhat later, Molisch (Bot. Ztg. 1905, 145) obtained the same, and several other pigments of the series, in crystalline condition on microscope-slides, and his work led Grafe (Sitzber. k. Akad. d. Wiss. Wien, 1906, 975; 1909, 1033; and 1911, 765) to attempt to obtain similar results on a large scale, but although he succeeded in procuring crystalline compounds in a number of cases, his chemical results have been largely disproved by the later work of Willstatter and his collaborators.

A considerable amount of investigation has been carried out upon the relationship existing between the anthocyan pigments and the yellow sap colouring matters—flavones and flavonols. Hope (Trans. Roy. Soc. Ed. 1836) developed ideas concerning this matter; Morot (*l.c.*), as also Filhol (*l.c.*), touched upon it, whereas Fremy and Cloëz (*l.c.*) criticised the drawing of conclusions as to such relationships whilst so little was known concerning the pigments involved. Martens (*l.c.*) suggested that the yellow and red sap-pigments have their origin in a faintly yellow-coloured substance produced in the sap of all plants and which passes by oxidation—particularly in light—into the yellow sap pigments, and that these, by further oxidation and light, pass in their turn into anthocyans. As the result of much botanical work, theories have been put forward by Wheldale, by Keeble, Armstrong, and Jones, and by others, which resemble that of Martens in that oxidation of the yellow sap pigments—flavones or flavonols—is considered to be one of the essential steps in the formation of anthocyan pigments. These ideas, which were becoming very generally accepted, have been disproved by Everest (Proc. Roy. Soc. 1914, B. 87, 444; and 1914, B. 88, 326), who succeeded in discovering the real relationship that exists between these two groups of pigments, and the manner in which the yellow sap pigments could be converted into anthocyanins. He showed that anthocyanidins are produced by reduction of flavonols, followed by spontaneous oxonium-salt formation and dehydration, a series of changes that may be expressed thus:—

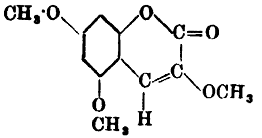

Flavonol.



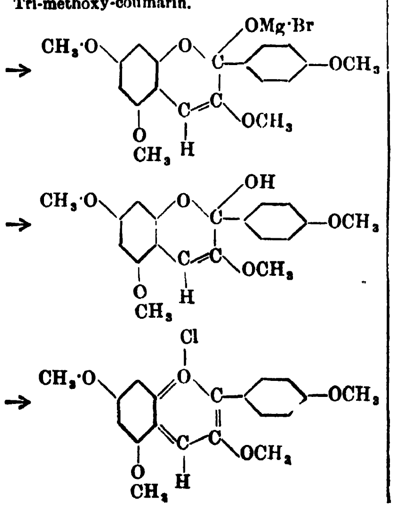
Anthocyan.

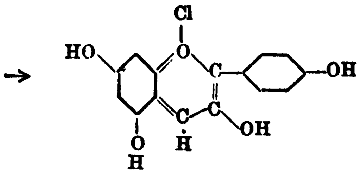
In like manner he obtained anthocyanins when glucosides of the flavonols were used. The evidence thus obtained by synthesis, and the structure proposed by Everest were in complete agreement with the results of analytical work, carried out independently and concurrently, by Willstätter and his collaborators in the extension of their work on the anthocyan pigments, and they, after repeating the work of Everest, confirmed it (Sitzber. d. K. Akad. Wiss. Berlin, 1914, 769), and in this way obtained synthetic cyanidin chloride and proved it to be identical with Willstatter and Everest's cyanidin chloride, obtained from the cornflower. In connection with the production of anthocyans from flavone derivatives, the following papers should also be noted, viz. Stein, J. pr. Chem. 1862 and 1863; Hlasiwetz und Pflaundler, Sitzber. Wiener Akad. Wiss. mat.-natw. Klasse. 1904; Watson, Chem. Soc. Trans. 1914, 105, 389; Combes, Compt. rend. 1913, 157, 1002, and 1454.

A further interesting synthesis of an anthocyanidin (pelargonidin) has since been carried out by Willstatter and Zechmeister (Sitzber. d. k. Preuss. Akad. d. Wiss. Berlin, 1914, 886), who made use of a totally different series of reactions which may be represented thus :—



Tri-methoxy-coumarin.

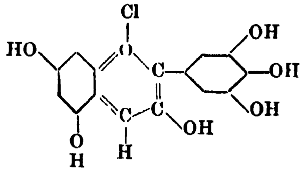




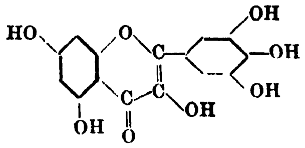
Pelargonidin chloride.

In this way the structure of all the anthocyan pigments thus far investigated has been established. It is interesting to note that all are derivatives related to flavonols, and in this connection Everest (*l.c.*) has pointed out that as flavones are also met with in plants, and that they yield red pigments on reduction, there is every reason to expect that anthocyans related to them may be brought to light as the result of further research.

It would seem that these pigments are formed in Nature from flavonol derivatives first produced in the plants. Direct chemical evidence of this has been obtained by Everest (Roy. Soc. Proc. 1918, B. 90, 251). He has isolated the anthocyan pigment *violanin*, a glucoside of delphinidin,

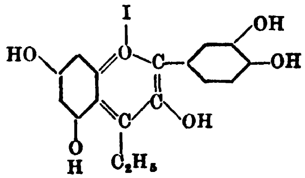


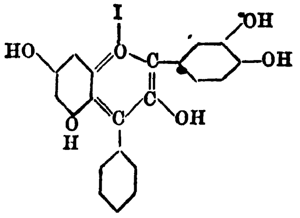
from the purple-black viola (Sutton's) 'Black Knight,' and has shown that, unless gossypetin is present, which appears unlikely, this pigment is accompanied in those flowers by a glucoside of myricetin :

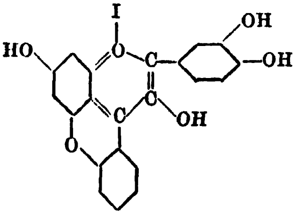


myricetin being the flavonol which would yield delphinidin by reduction.

Some interesting substitution derivatives of the anthocyan series have been prepared by Watson (Chem. Soc. Trans. 1914, 397; 1915, 1477), as the result of treating flavone and flavonol derivatives with various Grignard reagents. The following are typical examples of such compounds :—







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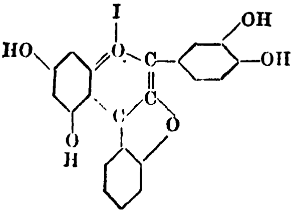


In 1913, in connection with their investigation of the cornflower pigment, Willstätter and Everest (*l.c.*) showed that all anthocyan pigments occurred in plants as glucosides (named by them *Anthocyanins*), and this generalisation has been supported and confirmed by all more recent work. In some few instances, however, *e.g.* in the black grape, a small percentage of sugar-free pigment (named *anthocyanidin*) has been found to accompany the glucoside.

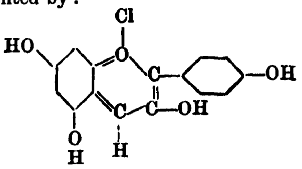
These authors introduced an important reaction whereby it is possible to determine whether a given anthocyan pigment is a glucoside or not. When a solution of the pigment in dilute aqueous acid (preferably *ca.* 0·5 p.c. HCl) is shaken with amyl alcohol (free from pyridine), the pigment, if a di-glucoside remains almost quantitatively in the aqueous layer, but if it is a mono-glucoside (rhamno-glucosides behave in this test very similarly to mono-glucosides), then an appreciable percentage of the pigment (*ca.* 10 p.c.) passes to the amyl alcohol, but this can be removed by shaking the alcohol layer repeatedly with fresh acid. If the pigment is a non-glucoside it passes quantitatively into the amyl alcohol, and shaking with fresh aqueous acid does not withdraw it.

The Anthocyanidins.

All the anthocyanins hitherto investigated are derivatives of three anthocyanidins, viz. *Pelargonidin*, *Cyanidin*, and *Delphinidin*, or of methyl ethers of these compounds.

Pelargonidin, which was first isolated in the form of its diglucoside, *pelargonin*, from the *Pelargonium zonale* (Meteor), may be obtained by the hydrolysis of that or any other of its glucosides isolated by Willstätter and his collaborators; such compounds occur in the following flowers, either alone or mixed with other anthocyan pigments, viz. purple-red summer aster, *Callistephus chinensis* (Nees), syn *Aster chinensis* (Linn.); the scarlet Salvia, *Salvia coccinea* (Linn.), and *S. splendens* (Sello.); the rose-coloured cornflower; scarlet-red gladiolas; and *Zinnia elegans* (Jacq.). The colouring matter is most readily isolated as the crystalline chloride.

Pelargonidin chloride $C_{15}H_{11}O_5Cl$, or 3 : 5 : 7-trihydroxy - 2 - *p* - hydroxyphenyl - 1 : 4 - benzo-pyranol anhydrochloride, has the structure represented by:



and crystallises with one molecule of water, this being removed only by drying in high vacuum at 105° C.

By the action of hydrochloric acid a related product is formed, the constitution of which is not settled. Pelargonidin chloride has been observed to yield three different crystalline forms: (i.) red tablets; (ii.) red-brown four-sided prisms; and (iii.) yellow-brown swallow-tail twin crystals (*cf.* Willstätter and Bolton, Annalen, 1915, 408, 42; and 1916, 412, 133); it is difficultly soluble in cold dilute acids, more soluble in warm; in alcohol it is very easily soluble. An acid solution of the chloride gives a blue colouration on addition of sodium carbonate solution, but ferric chloride does not produce any colour reaction. Unlike any other known pigment of this series, it shows two absorption bands, one in the yellow-blue portion of the spectrum, the other in the violet, the latter being the one not observed in other cases. The compound does not melt below 350° C.

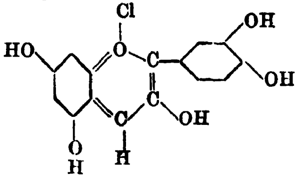
When decomposed by heating with concentrated caustic potash, or by fusion with potash, the decomposition products are mainly phloroglucinol and *p*-oxy-benzoic acid, but a small quantity of protocatechuic acid is also formed.

Pelargonidin **ψ-base** $C_{15}H_{12}O_6$, colourless prisms, not melting below 350° C., is formed when the chloride is heated with water (preferably by addition of a trace of sodium bicarbonate), the product extracted with ether, and crystallised from water. It is very easily soluble in alcohol, ether, and hot water; acidification of an aqueous solution with HCl causes the deposition of the chloride.

Pelargonidin chloride dyes wool (tin mordant) purple-red, and tannined cotton bluish-red; it does not dye unmordanted wool.

Cyanidin, first isolated by Willstätter and Everest (*l.c.*) from the blue cornflower pigment (cyanin), may be obtained by hydrolysis of this or any other of its naturally occurring glucosides, or from its methyl ether, peonidin, by demethylation. Glucoside-pigments derived from cyanidin have been isolated from, or detected in, the flowers of blue, and deep purple, cornflowers, *rosa gallica*, peony, chrysanthemum, dahlia (deep red), aster, poppy, *Zinnia elegans*, gladiolas (hybrid), *gaillardia bicolor*, *helenium autumnale*, *tulipa gesneriana*, *tropæolum majus*, and in the fruits, or berries, of the sweet cherry, sloe, cranberry, red currant, raspberry, and mountain ash. In some cases they are accompanied by derivatives of other anthocyanidins (*see* various papers by Willstätter and his collaborators).

Cyanidin chloride $C_{15}H_{11}O_6Cl$, 3 : 5 : 7-trihydroxy-2-*m* : *p* : dihydroxyphenyl-1 : 4-benzopyranol-anhydrochloride :



crystallises readily from 20 p.c. HCl, when its pure glucosides are hydrolysed by boiling with this reagent for three minutes, the crystals, long red-brown needles with metallic lustre, contain $1H_2O$, which is very difficult to remove, complete drying being only obtained at 105° C. in high vacuum. The anhydrous salt does not melt below 300° C.; if dried at 50° C. it melts at once if dipped into a bath at 220° C., but does not melt if put in at 200° C., and the temperature then gradually raised. It is very soluble in methyl, or ethyl alcohol; fairly soluble in dilute sulphuric acid; difficultly soluble in HCl. Neutral alcoholic or aqueous solutions lose their colour on standing owing to *pseudo*-base formation, acids reproduce colour, slowly if cold, rapidly if warm. The absorption spectrum shows one broad band with ill-defined edges.

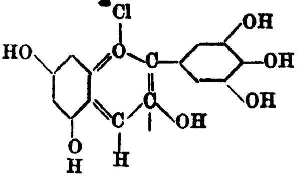
Cyanidin colour base, separates in crystalline condition when a hot concentrated solution of the chloride in alcohol is mixed with twice its volume of water (*cf.* Willstatter and Nolan, Annalen, 1915, 408, 13). It is fairly soluble in alcohol or pyridine.

Cyanidin pseudo base $C_{15}H_{12}O_7$, crystallises with one mol. H_2O when a dilute solution of the chloride in alcohol is mixed with twice its volume of water, warmed gently, then, after it has become colourless, evaporated *in vacuo*, extracted with ether, and the product crystallised from water. Readily soluble in water, alcohol, acetone, or glacial acetic acid, it is insoluble in benzol; with soda it gives a yellow colouration, with HCl cyanidin chloride is formed and crystallises out. When decomposed by means of fused alkali protocatechuic acid and phloroglucinol are produced.

Cyanidin chlorides dyes wool (tin mordant) blue-violet, cotton (tannined) violet, and unmordanted wool fine rose (Willstätter and Mallison).

Delphinidin, first obtained by Willstatter and Mieg (Annalen, 1915, 408, 61) from the pigment of purple wild delphinium (delphinin), may also be obtained by hydrolysis of violanin, the only other glucoside of delphinidin itself that has as yet been isolated, or by demethylation of its mono- or di-methyl ethers, several of which occur, as glucosides, in a variety of flowers and fruits.

Delphinidin chloride $C_{15}H_{11}O_7Cl$, 3 : 5 : 7-trihydroxy-2-*m* : *m* : *p* : trihydroxyphenyl-1 : 4-benzopyranol-anhydrochloride :



prepared by boiling the above-named glucosides with 20 p.c. HCl for two minutes, rarely separates pure from the hydrolysis as it is affected by concentrated hot HCl. Four distinct crystalline hydrates have been described by Willstätter and Weil (Annalen, 1916, 412, 178), viz. with $1H_2O$, $1\frac{1}{2}H_2O$, $2H_2O$, and $4H_2O$. W. and W.'s 'first hydrate' ($2H_2O$) separates from cold, aqueous alcoholic hydrochloric acid solutions (prepared by addition of 7–20 p.c. HCl to an alcoholic solution of the colour) when the alcohol is allowed to evaporate slowly; it forms aggregates of prismatic tablets; their 'second hydrate' ($1H_2O$) separates from cold, 3–5 p.c. hydrochloric acid as thin, sharply-cut, deep-violet, rhombic tablets; their 'third hydrate' ($4H_2O$) is deposited from 5 p.c. hydrochloric acid in the form of fine red-brown prisms and needles; their 'fourth hydrate' ($1\frac{1}{2}H_2O$) separates from hydrochloric acid containing more than 20 p.c. HCl, and is readily prepared by adding concentrated HCl to a solution of the colour in water, or dilute HCl, when an amorphous precipitate is first produced, but this slowly crystallises. All the above hydrates lose their water of crystallisation in a vacuum desiccator at room temperature. Of these hydrates the third and fourth appear most readily obtainable.

The chloride is easily soluble in methyl, or ethyl alcohol, and in water—the aqueous solution soon deposits violet flakes of the colour base—it is difficultly soluble in dilute sulphuric acid; ether extracts a portion of the colour from an aqueous solution, but shaking the ether extract with aqueous acid completely removes the colour. Addition of soda to an acid solution yields a fine blue colour; ferric chloride added to an alcoholic solution gives a pure blue, to an aqueous solution a violet colouration. When the chloride was treated with caustic potash (75 p.c.) at 250° C., Willstätter and Mieg obtained phloroglucinol, pyrogallol, and a small amount of gallic acid. The absorption spectrum consists of one band (yellow-green), which is fairly well defined.

Delphinidin sulphate, long prisms, from hot dilute sulphuric acid. *Iodide*, brown prisms, or leaflets, obtained by boiling the chloride with concentrated hydriodic acid and phenol. *Picrate*, fine red-brown needles and prisms, difficultly soluble in water. *Colour base*, amorphous violet precipitation deposited from neutral aqueous solutions of the chloride on standing. *Pseudo base* $C_{15}H_{12}O_8$, obtained by warming a dilute solution of the chloride with a trace of primary sodium phosphate, extracting with ether and recrystallising the product from water or ether; colourless prisms, no melting-point;

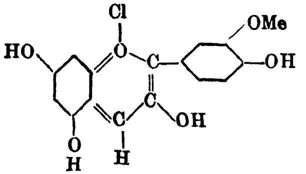
easily soluble in alcohol, acetone, ethyl acetate, or glacial acetic acid, less soluble in ether, insoluble in benzol; aqueous soda dissolves it with a yellow colour, aqueous hydrochloric acid converts it into the chloride.

Delphinidin chloride dyes mordanted wool (tin) blue, with violet tinge, tannined cotton blue-violet, and unmordanted wool violet.

METHYL ETHER OF CYANIDIN.

Peonidin, obtained by Willstätter and Nolan (Annalen, 1915, 408, 156) from the pigment of the deep violet-red peony, has been proved by them to be a mono-methyl ether of cyanidin.

Peonidin chloride $C_{16}H_{13}O_6Cl$ forms a crystalline hydrate with $1H_2O$, long red-brown needles, fairly soluble in cold water, very soluble in hot: very soluble in alcohol; very difficultly soluble in cold, easily soluble in hot 1 p.c. HCl, recrystallising well from this medium. With boiling hydriodic acid it yields cyanidin iodide; an acid solution yields a blue colour on addition of soda; ferric chloride gives no characteristic colour reaction From the ferric chloride test, together with the alkaline decomposition, which yielded evidence of a methyl ether of the phenolic acid, but no methyl ether of phloroglucinol, and further, as the result of Zeisel estimations, Willstatter and Nolan suggest the formulæ:



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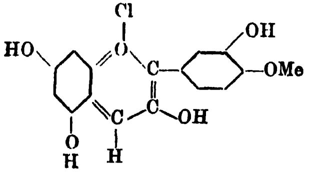


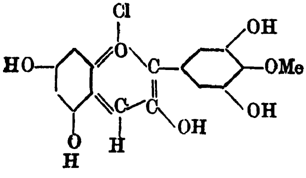
as probable for peonidin chloride.

Peonidin sulphate, brown-red needles, from 7 p.c. aqueous sulphuric acid.

METHYL ETHERS OF DELPHINIDIN.

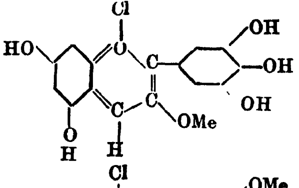
(a) *Mono-methyl Ethers.*

Ampelopsidin, isolated as the *chloride*, $C_{16}H_{13}O_7Cl$, by Willstatter and Zollinger (Annalen, 1916, 412, 216) from the pigment of the ampelopsis (*see* below), crystallises in prisms containing water of crystallisation, the amount of which has not yet been definitely settled, and probably has the structure:



Its investigation is not yet complete.

Myrtillidin has been obtained from the pigments *myrtillin* or *althein* (*see* below) by Willstätter and Zollinger (Annalen, 1915, 408, 83; and 1916, 412, 205) in the form of the crystalline *chloride* $C_{16}H_{13}O_7Cl$, clusters of deep brown prisms, or red-brown prismatic tablets, containing $1\frac{1}{2}H_2O$. Upon evidence obtained from alkaline decomposition, and consideration of the ferric chloride reaction, W. and Z. consider that the chloride has one of the following structures, viz.:



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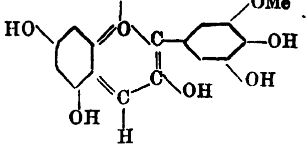
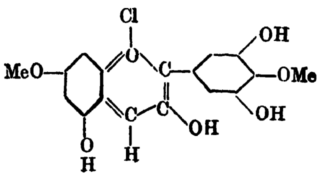


Petunidin, prepared by Willstätter and Burdick (Annalen, 1916, 412, 217) from the pigment of the cultivated petunia (*see* below), forms a crystalline *chloride* $C_{16}H_{13}O_7Cl$, yellow-brown prisms, or rhombic leaflets, containing $2H_2O$; it is closely related to, but somewhat different from, myrtillidin, and W. and B. consider that petunidin is represented by one, and myrtillidin by the other of the two structural formulæ set out above under myrtillidin, but at present a decision between them is not possible.

Anthocyanidin from Vitis Riparia Pigment. This product is probably one of the other possible mono-methyl ethers of delphinidin, but the work on it as yet is very incomplete.

(b) *Di-methyl Ethers.*

Malvidin. This compound has been isolated from the pigment of the wild mallow (*see* below) by Willstätter and Mieg (Annalen, 1915, 408, 122), who obtained it in the form of its crystalline *chloride* $C_{17}H_{15}O_7Cl$, deep-brown needles or prisms, often in rosettes, containing $2H_2O$, of which the last $1H_2O$ can only be removed at 105° C., in high vacuum. It does not melt below 300° C. Easily soluble in methyl or ethyl alcohol, but the solution in methyl alcohol soon deposits a crystalline precipitate; fairly soluble in amyl alcohol, it is difficultly soluble in dilute sulphuric acid. It gives no ferric chloride reaction, from which, and the fact that they obtained evidence from alkaline decomposition, that one MeO group was in each of the benzene nuclei, W. and M. have put forward the structural formulæ:



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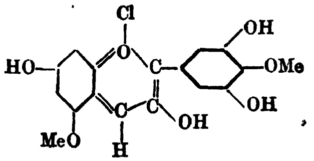
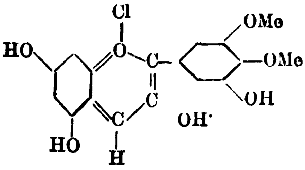


for this compound.

Picrate, red-brown needles, difficultly soluble in water.

Oenidin has been prepared by Willstatter and Zollinger (Annalen, 1915, 408, 83; and 1916, 412, 195) from the pigment of the black grape, or red wine. It appears to exist in black grapes, with the glucoside oenin.

Oenidin chloride $C_{17}H_{15}O_7Cl$ crystallises in deep brown prisms or needles, with bronze reflex, containing $1\frac{1}{2}H_2O$, of which the last half molecule is not removed until heated to 135° C. in high vacuum. It is readily soluble in water, in methyl or ethyl alcohol, in dilute HCl or dilute sulphuric acid; an acid solution becomes violet on addition of soda, but blue with caustic soda. From the products of alkaline decomposition (which showed that no MeO group was present in the portion of the molecule which yielded phloroglucinol, but at least one was in the other phenyl group), and the absence of a ferric chloride reaction, Willstatter and Zollinger have proposed the following formulæ for this compound, viz.:



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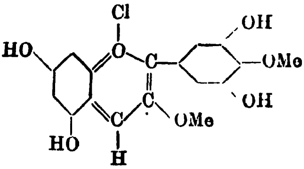


Picrate, fine deep red prisms, very difficultly soluble in water.

All the above-mentioned mono- or di-methyl ethers of delphinidin yield delphinidin iodide when boiled with concentrated hydriodic acid.

THE GLUCOSIDES (ANTHOCYANINS).

The glucoside members of this group are the pigments producing the reds, purples, and blues which form so noticeable a part of the colourings of flowers, fruit, and autumn leaves. In many instances one pigment may produce all these shades, the colour being dependent on the condition of the cell sap; thus cyanin, as its potassium salt, is the blue of the blue cornflower; as the colour base, it is the purple of the deep purple kinds of the same plant, whereas the same pigment in combination with plant acids gives the red colour to *Rosa gallica*.

Yellow sap pigments, flavone derivatives, being but very faintly coloured unless present as alkali salts, rarely play any great part in the colouration of flowers, except in the production of pale yellows, as in the primrose, or together with anthocyanins, where these are not strong, of pale peach-colour effects; on the other hand, the strongly yellow, or orange, carotinoids produce—beyond the colourations for which they are solely responsible—orange and brown shades when present together with anthocyans.

Owing to the varying sap conditions which occur, and their effect on the pigments, it is not easy, and is often impossible, to obtain, by means of mere observation, any accurate estimation of the quantity of an anthocyan pigment present in a flower; moreover the shades produced by different anthocyanins often resemble one another so closely as to make discrimination between them impossible (*cf.* Willstätter and Mallison Annalen, 408, 147).

Methods of Isolation.

Willstätter and Mallison (*l.c.*) summarise the various methods used for the isolation of anthocyanin pigments thus:—

I. Precipitation and crystallisation of the chloride, *e.g. pelargonin.*

II. Special purification of the pigment followed by crystallisation of the chloride, *e.g.*

(*a*) *Cyanin* (i). from blue cornflower, by purification of the alkali salt by precipitation with alcohol from aqueous solution, followed by conversion to the chloride and fractional purification from alcohol by ether;

(ii.) from rose, or peony, by long standing with a mixture of glacial acetic acid, methyl alcohol, and HCl, whereby impurities are hydrolysed or acetylated.

(*b*) *Myrtillin*, by repeated purification from aqueous solution by HCl.

(*c*) *Delphinin* (i.) by purification of violet colour base from dilute alcohol, soluble by addition of concentrated alcohol;

(ii.) by gently warming with HCl, whereby impurities are hydrolysed, but not the delphinin.

III. Precipitation of the pigment as crystalline picrate, followed by conversion of the pure picrate to chloride, *e.g. Oenin, myrtillin, idaein.*

1. *Derivatives of Pelargonidin.*

Pelargonin, a diglucoside of pelargonidin, the pigment of the scarlet *pelargonium zonale*, was so named by Willstatter and Bolton (Annalen, 1915, 408, 42), to whom we owe our chemical knowledge of this pigment. *Cf.* earlier workers, Griffiths (*l.c.*), Molisch (*l.c.*), and Grafe (*l.c.*). Willstätter and Bolton have also shown that this colouring matter occurs in the pink cornflower, and the cactus dahlia (*ibid.* p. 149).

Pelargonin' chloride $C_{27}H_{31}O_{15}Cl$ crystallises in long red needles, containing $4H_2O$, all of which is lost in vacuum desiccator at room temperature. When anhydrous it softens at 175° C., melts at 180° C. (decomposed). Not very soluble in water, methyl, or ethyl alcohol, its alcoholic solutions show characteristic greenish-yellow fluorescence. It is optically active. W. and B. give $[\alpha]_D = -291°$, $[\alpha]_{614} = -180°$; the salt shows an absorption spectrum consisting of one broad band.

Basic chloride

$$(C_{27}H_{31}O_{15}Cl)_2{\cdot}(C_{27}H_{30}O_{15}){\cdot}12H_2O,$$

deep violet microscopic needles, obtained by boiling the normal chloride with 96 p.c. alcohol for a few minutes. *Acetate*

$$(C_{27}H_{30}O_{15})_2{\cdot}(C_{27}H_{30}O_{15}{\cdot}C_2H_4O_2),$$

fine red needles from a solution of the base (*see* below) in warm glacial acetic acid. *Pelargonin base* $C_{27}H_{30}O_{15}$, amorphous, difficultly soluble in water or alcohol, obtained by the action of a small quantity of water on the normal chloride.

Salvianin (Willstatter and Bolton, Annalen, 1916, 412, 113), as yet only obtained crystalline as picrate, is the pigment of the scarlet *Salvia splendens*, in which it occurs to the extent of *ca.* 6 p.c. The *chloride* (not crystalline) when completely hydrolysed, yields pelargonidin chloride (*ca.* 36 p.c.), glucose (*ca.* 30 p.c.), and malonic acid (*ca.* 25 p.c.). It behaves abnormally in distribution between amyl alcohol and aqueous acid, and it appears possible that the glucose is present in a dehydrated form $C_6H_{10}O_5$. Careful hydrolysis with HCl appears to remove the malonic acid, yielding a new pigment *Salvin chloride*, probably $C_{27}H_{27}O_{13}Cl$ (a diglucoside of pelargonidin $-2H_2O$), which shows the same abnormal distribution as the previous compound; this was obtained in a crystalline condition by W. and B. Further gentle hydrolysis then yields a true diglucoside of pelargonidin which was named *Salvinin chloride* $C_{27}H_{31}O_{15}Cl$; this body shows normal distribution for a diglucoside anthocyanin, whilst by further careful hydrolysis it yields a mono-glucoside of pelargonin and glucose (1 mol.), whilst finally the monoglucoside yields pelargonidin and glucose. W. and B. have not completed their investigation of these pigments, and the names they have used are stated to be tentative.

Callistephin, a mono-glucoside of pelargonin, is present together with asterin (a cyanidin glucoside) in purple-red asters (*Callistephus chinensis* (Nees), syn. *Aster chinensis* (Linn.), from which it was isolated by Willstatter and Burdick (Annalen, 1916, 412, 149). It was separated from asterin by fractional precipitation from alcohol by ether, and recrystallised from aqueous alcoholic hydrochloric acid. *Chloride*

$$C_{21}H_{21}O_{10}Cl,$$

fine orange-red needles containing 2–2½ H_2O; easily soluble in water, alcohol, or dilute acids (HCl, H_2SO_4). Acid solutions become red-violet with alkalis; it gives no ferric chloride reaction; unlike pelargonin it does not show fluorescence in alcoholic solution.

Pelargonenin, a mono-glucoside of pelargonidin, has been prepared by Willstatter and Bolton (Annalen, 1916, 412, 133) by partial hydrolysis of pelargonin with cold concentrated HCl, any pelargonidin produced being removed by means of amyl alcohol, and the chloride crystallised from warm 2 p.c. HCl. *Chloride* $C_{21}H_{21}O_{10}Cl$, scarlet-red needles, probably containing 2½ mols. water, sparingly soluble in water, very difficultly soluble in dilute HCl; its alcoholic solutions show strong fluorescence.

2. *Derivatives of Cyanidin.*

Cyanin, the pigment of blue or purple cornflowers, also occurs in *Rosa gallica*, and deep red dahlia flowers; it is a diglucoside of cyanidin. Willstätter and Everest (Annalen, 1913, 401, 189) first obtained it in a pure condition, as the crystalline chloride, from the blue cornflower; it is, however, more readily prepared from *Rosa gallica* (W. and Nolan, Annalen, 1915, 408, 1), or the deep red dahlia (W. and Mallison, Annalen, 1915, 408, 147). The *chloride* $C_{27}H_{31}O_{16}Cl$, red-brown rhombic leaflets containing 2½ mols. of water can only be completely dried at 105° C. in high vacuum. Air-dried it is very difficultly soluble in water, acetone, or chloroform, difficultly soluble in cold alcohol or dilute HCl, insoluble in benzol. In 7 p.c. sulphuric acid it is fairly soluble, but the sulphate separates out from the solution. Soda added to an acid solution gives a pure blue; ferric chloride gives a fine blue in alcohol, violet in water. It shows a single absorption band covering the green and blue; it is optically active. Willstätter and Nolan give, for white light, $[\alpha] = -258°\ (\pm 10°)$. *Picrate,* red needles, very soluble in water. *Cyanin potassium salt,* the blue pigment of the cornflower, was obtained crystalline, but not free from NaCl, by Willstatter and Everest, after purification by dialysis. It is very soluble in water, insoluble in alcohol; its blue aqueous solutions become colourless on standing owing to formation of *pseudo*- base, whereas in 20 p.c. NaCl solution the colour is stable for months.

Mekocyanin, isolated by Willstatter and Weil (Annalen, 1916, 412, 231), is one of the pigments of the poppy (*Papaver rhœas* (Linn.)), and a diglucoside of cyanidin. Its isolation is difficult, and involves a separation from a second pigment which has not yet been investigated. The *chloride* $C_{27}H_{31}O_{16}Cl$, crystallises in needles containing $3H_2O$, 2 mols. being readily removed, the third only at 105° C. in high vacuum. Very easily soluble in water, dilute HCl, fairly soluble in methyl, difficultly soluble in ethyl alcohol, insoluble in acetone, but soluble in a mixture of acetone and water; its reactions closely resemble those of cyanin chloride. *Ferrocyanide,* fine red-brown needles, prepared by adding potassium ferrocyanide to a solution of the chloride in very dilute HCl; fairly soluble in water, sparingly soluble in alcohol.

Mekocyanin chloride, when carefully hydrolysed, first yields a mono-glucoside (identical with *Chrysanthemin*) and 1 mol. glucose, then by further hydrolysis cyanidin and a further molecule of glucose.

Keracyanin, a rhamno-glucoside of cyanidin, is the pigment of the sweet cherry (*Prunus avium* (Linn.)), and has been isolated by Willstätter and Zollinger (Annalen, 1916, 412, 164) from the skins of that fruit; the purification is tedious, and not final in form. The *chloride* $C_{27}H_{31}O_{15}Cl$ occurs in two forms, fine needles containing $4H_2O$, and short brown-yellow prisms containing $3H_2O$. The salt is easily soluble in methyl alcohol, fairly soluble in ethyl alcohol, difficultly soluble 0·01–0·1 p.c. HCl, but easily soluble 1 p.c. HCl, then less soluble as the concentration of HCl increases.

Prunicyanin, isolated by Willstätter and Zollinger (*l.c.*) from the skins of the sloe (blackthorn, *Prunus spinosa* (Linn.)) is a rhamno-glucoside of cyanidin, closely resembling mekocyanin; its investigation is not yet complete. *Chloride,* not obtained crystalline, but as small spherical particles; yields, on hydrolysis, cyanidin chloride, rhamnose, and a hexose (not yet identified), in approximately molecular proportions.

Asterin, one of the pigments of the purple-red aster (*cf.* Callistephin), has been isolated by Willstätter and Burdick (*l.c.*), it is a monoglucoside of cyanidin. The *chloride* $C_{21}H_{21}O_{11}Cl$, red-brown prisms, containing $1\frac{1}{2}H_2O$, closely resembles chrysanthemin chloride in its reactions, but differs greatly from it in solubilities in dilute acids.

Chrysanthemin, isolated by Willstätter and Bolton (Annalen, 1916, 412, 136), a monoglucoside of cyanidin, is the pigment of the deep red chrysanthemum (*Chrysanthemum indicum* (Linn.)). The *chloride* $C_{21}H_{21}O_{11}Cl$, red-violet leaflets containing $1\frac{1}{2}H_2O$, resembles Idæin chloride in many respects. *Picrate*, thin red prisms, difficultly soluble in water, sinters at 155° C., melts at 165° C. (decomp.).

Idæin, the pigment of the cranberry (*Vaccinium vitis idæa* (Linn.)), has been isolated by Willstätter and Mallison (Annalen, 1915, 408, 15); it is a mono-galactoside of cyanidin. The *chloride* $C_{21}H_{21}O_{11}Cl$, brown-red prisms containing $2\frac{1}{2}H_2O$, melts at 210° C. (frothing). Easily soluble in water or alcohol, almost insoluble in dilute HCl; ferric chloride gives a blue colour in alcohol, a violet in water. It is optically active, W. and M. give: $[\alpha]_C = -219°$ (±15°). *Picrate*, red needles, more soluble in hot than in cold water. *Sulphate*, brown rhombic crystals from 7 p.c. sulphuric acid.

Peonin, a diglucoside of peonidin, the pigment of the deep violet-red peony, has been isolated by Willstatter and Nolan (Annalen, 1915, 408, 136). The *chloride* $C_{28}H_{33}O_{16}Cl$, red-brown needles containing $5H_2O$, m.p. 165° C.; for complete drying 100° C. in high vacuum is necessary. Very easily soluble in water, easily soluble in alcohol, insoluble in acetone; it resembles cyanin in many reactions, but ferric chloride gives no characteristic reaction. It is optically active. W. and N. give, for white light, $[\alpha] = -191°$ (±5°). *Picrate*, red-brown needles, from water.

3. *Derivatives of Delphinidin.*

Delphinin, the pigment of the purple wild delphinium (*Delphinium consolida* (Linn.)), has been isolated by Willstatter and Mieg (Annalen, 1915, 408, 61), and is a complex derivative of delphinidin. Unlike all other known anthocyan pigments, it does not appear to form a *pseudo*-base when its neutral aqueous solution is allowed to stand, or is warmed. Although the free colour base can be isolated by fractional precipitation with alcohol, the compound is best isolated as the *chloride* $C_{41}H_{39}O_{21}Cl$, which appears to crystallise with 12 mols. of water, of which, however, only 10 can be removed even by drying in high vacuum at 130° C. It forms deep-red prismatic tablets or prisms, and dried as above sinters at 150°–160° C., then melts at 200°–203° C. (decomp. and swelling). Easily soluble in methyl alcohol, difficultly soluble in ethyl alcohol, in dilute HCl (over 0·5 p.c.), or in dilute sulphuric acid; water rapidly produces the colour base; ferric chloride gives a blue colouration in aqueous or alcoholic solution; sodium carbonate, to an acid solution, gives a fine blue. The salt is optically active, W. and M. give $[\alpha]_C = -1364°$ (±150°); $[\alpha]_{614} = -2273°$ (±150°); its absorption spectrum consists of one broad band. When hydrolysed it yields delphinidin chloride (1 mol.), glucose (2 mols.), and *p*-oxy-benzoic acid (2 mols.). *Colour base*, produced by the action of water on the chloride, and recrystallised from dilute alcohol by slow increase in the concentration of the alcohol, forms rosettes of violet needles. *Picrate*, red-brown flocculent precipitate, very difficultly soluble in water.

Violanin, isolated by Willstätter and Weil (Annalen, 1916, 412, 178) from the blue-black pansy, and by Everest (Roy. Soc. Proc. 1918, B, 90, 251) from the purple-black viola, is a rhamno-glucoside of delphinidin. The *chloride*, probably $C_{27}H_{31}O_{16}Cl$, forms deep red hexagonal or tetrahedral plates or tablets containing about 16 p.c. of water. Its solubility in aqueous HCl decreases up to *ca.* 12 p.c. HCl, but increases again after *ca.* 20 p.c. HCl is reached; it is almost insoluble in dilute sulphuric acid; with soda an acid solution gives a blue colour; ferric chloride gives pure blue in alcohol, or in water. Hydrolysis yields delphinidin chloride, glucose, and rhamnose in approximately molecular proportions. *Picrate*, cherry-red needles, fairly soluble in water.

Ampelopsin, the pigment of the berries of *Ampelopsis quinquefolia* (Michx.), *Vitis hederacea* (Ehrh.), has been isolated by Willstätter and Zollinger (*l.c.*); it is a mono-glucoside of ampelopsidin. The *chloride* $C_{22}H_{23}O_{12}Cl$ crystallises in prisms containing $4H_2O$; easily soluble in methyl or ethyl alcohol; sodium carbonate gives violet, caustic soda a blue colouration when added to an acid solution; ferric chloride only produces a weak reaction.

Myrtillin, the pigment of the bilberry (*Vaccinium myrtillus* (Linn.)), has received attention from earlier workers—*cf.* Andree (Arch. Pharm. 1879, 13, 90), Heise (*l.c.*), and others—but its isolation is due to Willstatter and Zollinger (Annalen, 1915, 408, 83; and 1916, 412, 205). It is a mono-glucoside of myrtillidin. The *chloride* $C_{23}H_{23}O_{12}Cl$, forms red brown tablets containing $4H_2O$, which is only lost completely in high vacuum at 105° C. It is very soluble in water, or methyl alcohol, but less soluble in ethyl alcohol. Ferric chloride gives a blue in alcohol, violet in water; sodium carbonate produces blue-violet, caustic soda blue when added to an acid solution. Its absorption spectrum shows one band with ill-defined edges. *Picrate*, red needles, difficultly soluble in water.

Althein, the pigment of the black hollyhock (*Althaea rosea* (Cav.)), has been isolated and described by Willstätter and Martin (Annalen, 1915, 408, 100; *cf.* Polyt. Zentralblt. 1860, 1540; Glan, *l.c.*; and Grafe, *l.c.*). The *chloride* $C_{22}H_{23}O_{12}Cl$ which crystallises in brown-red prisms containing $4H_2O$, is easily soluble in water, dilute HCl, dilute sulphuric acid, or in methyl or ethyl alcohol, but almost insoluble in glacial acetic acid; ferric chloride gives a violet-blue colour in alcohol, and violet in water; sodium carbonate produces a blue colour when added to an acid solution. It is optically active. W. and M. give $[\alpha]_{623} = -655°$; $[\alpha C] = -545°$; $[\alpha]_{692} = -291°$. The *picrate* is crystalline and difficultly soluble.

Petunin, the colouring matter of the purple-blue petunia 'Karlsruher Rathaus,' was isolated by Willstätter and Burdick (Annalen, 1916, 412, 217); it is a diglucoside of petunidin. The *chloride* $C_{28}H_{33}O_{17}Cl$ crystallises in prisms containing $2H_2O$, which sinter at 165° C. and melt at 178° C. It is difficultly soluble in dilute HCl, fairly soluble in dilute sulphuric acid, easily soluble in methyl, but less so in ethyl alcohol; ferric chloride gives a poor blue colour in alcohol, or in water; sodium carbonate turns an acid solution blue.

The anthocyanin from the skins of the berries of *Vitis riparia* is a mono-glucoside of a delphinidin mono-methyl ether, but, though obtained in a finely crystalline condition by Willstätter and Zollinger (*l.c.*), it has not yet been completely investigated.

Malvin, isolated by Willstätter and Mieg (Annalen, 1915, 408, 122) from the flowers of the wild mallow (*Malva silvestris* (Linn.)), is a diglucoside of malvidin. The *chloride* $C_{29}H_{35}O_{17}Cl$ forms long red prisms, or bundles of needles, containing $8H_2O$, all of which is lost at room temperature in vacuum desiccator. Difficultly soluble in dilute HCl, or dilute sulphuric acid. it is easily soluble in methyl alcohol, but less so in ethyl alcohol. It gives no ferric chloride reaction; sodium carbonate turns an acid solution blue. *Picrate*, red needles, fairly soluble in water.

Oenin, the pigment of black grapes, and of red wine, has been the subject of many investigations from the time of Berzelius (1837), but Willstatter and Zollinger (Annalen, 1916, 412, 198) first isolated and described this substance, which is a mono-glucoside of oenidin. The *chloride* $C_{23}H_{25}O_{12}Cl$, deep red prisms containing 4 or $6H_2O$, is easily soluble in water, fairly soluble in dilute HCl, easily soluble in dilute sulphuric acid, fairly soluble in ethyl, and more so in methyl alcohol. With ferric chloride it gives no colouration; with sodium carbonate an acid solution becomes blue. It is optically active, and W. and Z. give $[\alpha]_{627} = -542°$ ($\pm 60°$); and $[\alpha]_C = -421°$ ($\pm 30°$); its absorption spectrum shows one band. *Picrate*, bundles of carmine-red needles, difficultly soluble in cold water, easily soluble in hot.

The colour reaction with alum, described by Willstätter and collaborators for many of the pigments of this series, is due to traces of iron in the reagent (A. E. Everest, Proc. Roy. Soc. 1918, B. 90, 260).

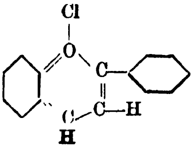
Dyeing Properties of the Anthocyans.

The anthocyanins and anthocyanidins are capable of dyeing not only on mordanted wool, but also on tannined cotton, and indeed some are described by Willstatter as capable of dyeing unmordanted wool.

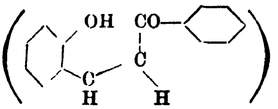
The shades obtained vary from rose to violet and blue, and are fast to light, but very unstable to most reagents, and, owing to pseudo-base formation, even to water.

The substances prepared by Watson, and mentioned above, resemble the natural anthocyans in tinctorial properties, though some of them show very much greater fastness, and in this respect approach the requirements of technical practice.

Everest and Hall (private communication) have confirmed the fact that the affinity of the anthocyans for tin-mordanted wool is connected with the phenolic OH groups present in them. They have also shown that their affinity for tannined cotton is independent of these groups, but dependent upon the presence of the pyrylium ring. Thus the compound:



which is the parent of all the anthocyanidins, has no affinity for tin-mordanted wool, but readily dyes tannined cotton. On the other hand the compound from which the above substance is formed by closing the pyrylium ring



has no dyeing properties.

Further observations have also shown that the compounds which Watson described as dyeing tin-mordanted wool also fall into line in respect of tannined cotton, which they dye very readily.

It is not at all impossible that a new series of technically useful colours for tannined cotton may result from further research in this field.

For fuller details the original papers, or The Natural Organic Colouring Matters, Perkin and Everest (Series of Monographs, Longmans), should be consulted. A. E. E.

ANTHOKIRRIN. The yellow crystalline matter of the flowers of the yellow toadflax (*Linaria vulgaris*). Formerly used as a dyeing material, but the colour is not permanent.

ANTHOKYAN. The expressed juice of the sweet or purple violet (*Viola odorata*), gently heated to 89°, then skimmed, cooled, and filtered. A little rectified spirit is then added, and the following day the whole is again filtered. Used to make syrup of violets, and to colour and flavour liqueurs.

ANTHOPHACIN. A term given by Möbius (Chem. Zentr. 1901, i. 190) to the brown colouring matter of flowers.

ANTHRACENE $C_{14}H_{10}$. Discovered by Dumas and Laurent in the highest boiling portion of coal tar, and termed by them *paranaphthalene* (Annalen, 5, 10); further examined by Laurent, who re-named it *anthracene* (Annalen, 34, 287); first obtained pure, and its composition determined, by Fritzsche (Annalen, 109, 249), and more exactly studied by Anderson (Annalen, 122, 294; Chem. Soc. Trans. 15, 44).

Occurrence.—Anthracene is one of the products of the destructive distillation of coal, and is found in the tar; the average yield of the pure hydrocarbon is about 0·3 p.c. of the tar obtained.

A new source of anthracene has been announced (Dingl. poly. J. 246, 429) in the tar obtained when the residue, left after the illuminating oils have been distilled from Baku petroleum, is allowed to fall on pumice in red-hot iron retorts. 1000 kilos of naphtha residue under these conditions yield 500 c.m. of gas, used to heat the retorts, and 300 kilos. of tar, containing about 0·2 p.c. of pure anthracene. The supply of the naphtha residue is, however, too limited to render anthracene from this source a serious competitor with that from coal tar.

According to Elliott (Amer. Chem. J. 6, 248), the tar obtained in the manufacture of gas by the destructive distillation of light petroleum naphtha boiling below 150° contains 2·63–2·90 p.c. of anthracene. A remarkable production of anthracene, during the distillation of the higher-boiling portions of crude phenol, has been observed by Köhler (Ber. 18, 859).

Anthracene is obtained by the distillation of rhein with zinc-dust (Oesterle and Tesza, Arch. Pharm. 1908, 432), but this production is of no commercial value.

Preparation (Auerbach, Das Anthracen und seine Derivate; Kopp, J. 1878, 1187; Perkin, Journ. Soc. Arts. 27, 572; Lunge, Coal Tar and Ammonia).—Anthracene is obtained from the 'green grease' which forms the last portion of the 'heavy oil' or 'dead oil' of the tar distiller; this at first is greenish-yellow in colour, but turns more brown by the action of the air, and becomes semi-solid on standing, owing to the separation of solid substances. It contains, amongst other substances, naphthalene, methyl naphthalene, anthracene, methyl anthracene, phenanthrene, chrysene, carbazol, and acridine, together with hydrides of anthracene and phenanthrene and other high-boiling liquids. When no further separation occurs, the mass is subjected to filtration, either in a centrifugal machine or a filter press, first in the cold and finally at 40° (Gessert, Dingl. poly. J. 196, 543); or is filtered through strong linen bags, and afterwards submitted to hydraulic pressure in a press so arranged that the plates can be heated with steam and the cake hot-pressed. A notable quantity of anthracene remains dissolved in the expressed oil, and especially in the portions separated when the temperature is raised, and is recovered by redistilling and working up the product as just described. The hard yellowish-green cake obtained, containing 25–40 p.c. of pure anthracene, is ground to a fine powder in mills and heated with coal-tar naphtha (b.p. 80°–100°), solvent naphtha (b.p. 120°–190°), creosote oil, or petroleum spirit (b.p. 70°–100°), in large iron vessels provided with stirrers. Petroleum spirit is to be preferred (Perkin), since it dissolves less anthracene whilst the impurities are sufficiently soluble in it to be removed if the quantity of solvent employed is 2–3 times as great as that of the anthracene to be purified. Solvent naphtha, consisting essentially of xylenes, pseudo-cumene and mesitylene, is extensively employed, as phenanthrene is much more soluble than anthracene in this solvent. It does not, however, remove the carbazole, which is usually present to the extent of 14–18 p.c. When creosote oil is used, it must be free from naphthalene; the advantage of using creosote oil is that it dissolves out the methyl anthracene, the anthracene being practically insoluble therein. The residue contains from 45–50 p.c. of the hydrocarbon, but inasmuch as it is not readily reduced to powder, and unless finely divided is only slowly attacked by oxidising agents, it is sublimed by passing steam, heated at 220°–240°, over the melted product, and condensing the vapours in a chamber by jets of water. The anthracene thus obtained is in leafy masses, containing from 50–60 p.c. of the hydrocarbon, the chief impurities consisting of carbazole (10–12 p.c.), phenanthrene, pyrene, chrysene, and other hydrocarbons, together with small quantities of phenols of high boiling-point, and of acridine; it can readily be ground to a paste, and is now sufficiently pure for conversion into anthraquinone by oxidation. If, however, dichloranthracene is required, further purification is necessary; this can be effected by distillation with caustic potash, whereby impurities such as carbazole and bodies of a phenolic character are retained, and anthracene, together with phenanthrene, distils over with no greater loss than occurs if the 60 p.c. product is distilled alone; caustic soda cannot be substituted for the potash, since it produces no purification of any consequence. Instead of distilling washed anthracene, (100 parts) with caustic potash, Perkin employs a mixture of Montreal potash (30 parts), which usually contains potassium hydroxide in considerable quantities, and caustic lime (6 parts). Unless lime is used, the residue in the retorts forms a hard cake, which can be removed only with difficulty. Hydrogen is evolved during the distillation. The distillate is freed from phenanthrene by washing with coal-tar naphtha, and the residue is a very pure anthracene. This production of phenanthrene, even from anthracene which has been freed from this impurity by extraction with solvents previous to distillation with caustic potash, is noteworthy and points to the probable existence of molecular compounds of phenanthrene with other of the impurities of the washed anthracene, which are destroyed during the distillation with caustic potash. This process of Perkin has been subjected to considerable criticism. According to Auerbach, a loss of anthracene to the extent of 10 p.c. occurs, and this, added to the cost of fuel employed, renders it the most costly method of purification yet devised. The great advantage of the method, however, is that it brings anthracenes of different origins to a similar condition of purity; even pitch anthracene—obtained by the distillation of gas-tar pitch in iron retorts with the aid of super-heated steam, and generally unsuitable for purification owing to the difficulty of removing higher hydrocarbons associated with it—works perfectly well after it has been subjected to this process.

Many modifications in the method of purifying crude anthracene have been introduced. A method based on the far greater solubility of the impurities in mixtures of aniline, pyridine, or quinoline bases, has been patented by the Chemische Fabriks-Actiengesellschaft in Hamburg (D. R. P. 42053 of April 15, 1887). The crude anthracene is dissolved at 100° in 1½–2 times its weight of a dehydrated and rectified mixture of tar bases (pyridines) separated from the light oil obtained in tar distillation (compare D. R. P. 34947 and 36372), and the solution, on cooling, yields a crystalline separation of anthracene almost free from carbazole and its homologues. The patentees state that a 33 p.c. anthracene dissolved in 1·75 times its weight of pyridine bases yields on crystallisation an 82·5 p.c. anthracene, whilst when dissolved in twice its weight of a mixture of equal parts of pyridine bases and benzene, it yields an 80 p.c. anthracene, and in twice its weight of a mixture of equal parts of benzene and aniline a 75 p.c. anthracene. The recovery of the anthracene contained in the mother liquors offers no special difficulty.

Remy and Erhart (D. R. P. 38417 of Jan. 19, 1886) have proposed crystallisation from oleic acid as a means of purification of crude anthracene. The difficulty of recovering the anthracene contained in the mother liquors would seem, however, to deprive this method of technical importance.

Graham (Chem. News, 33, 99, 168) has devised a method for recovering anthracene from the filtered oils used in its purification.

The Farbenfabriken vorm. Friedr. Baeyer & Co. (D. R. P. 68174; Eng. Pat. 6539; J. Soc. Chem. Ind. 1893, 439) employ liquid sulphur dioxide, which dissolves the impurities of crude anthracene, but very little anthracene itself. 600 kilos. crude anthracene is mixed in a wrought iron agitator with 2400 kilos. liquid sulphur dioxide, first exhausting the air and then allowing the sulphur dioxide to enter. The reaction having ceased, the mass is forced by its own vapour pressure into an iron steam-jacketed, filtering tower, where anthracene of 70–80 p.c. remains behind. The mother liquor is distilled, the sulphur dioxide being collected and recondensed by means of an air-compressor.

Another patent of the same firm (D. R. P. 78861; Eng. Pat. 7862; J. Soc. Chem. Ind. 1895, 361) recommends the use of acetone or other fatty ketones as a purifying agent. 560 kilos. crude anthracene is stirred in a steam-jacketed cylinder with 750 kilos. acetone for an hour. After cooling the separated anthracene is filtered and washed with 375 kilos. acetone. The second liquor is used over again, and the first is distilled to recover the acetone. From crude stuff containing 34 or 35 p.c. anthracene, an article of 82 p.c. is easily made, and only a few per cent. anthracene remain in the residue after distilling off the acetone. The acetone may be used in the form of 'raw acetone' or 'acetone oils.'

Welton (Eng. Pat. 27559; D. R. P. 113291; J. Soc. Chem. Ind. 1900, 139) purifies crude anthracene by means of liquid (anhydrous) ammonia, which dissolves out most of the impurities, but not the anthracene itself.

Luyten and Blumer (Eng. Pat. 14892; D. R. P. 141186; J. Soc. Chem. Ind. 1901, 796) state that when anthracene is purified by solvents such as naphtha, acetone, &c., the presence of tar oil in the crude anthracene is beneficial. 25 parts of drained crude anthracene are heated with 35 parts of naphtha until the temperature is near that of the solvent. On cooling, the anthracene crystallises out and is filtered and washed with a little of the solvent. It is dried by heating to fusion, and distilling off the solvent; 80 p.c. anthracene is obtained by this method.

The Aktien Gesellschaft für Theer und Erdöl Industrie (D. R. P. 111359; Eng. Pat. 7868; J. Soc. Chem. Ind. 1899, 750) heat crude anthracene to fusion, and allow it to cool until 50 p.c. has crystallised, when the mother liquor is run off and again allowed to crystallise. The second crop can be raised to the value of the first (45–50 p.c.) by another fusion. This product is again fused and treated with caustic potash lye (50 p.c.) in quantity sufficient to react with the carbazole present. When the reaction is complete, the mass separates into two layers, the lower part being potassium carbazole. The upper anthracene layer is run into its own volume of 90's benzol, which dissolves any phenanthrene. The anthracene is pressed or centrifuged, and again washed with the same solvent, and is obtained as a pale-brown powder. By this means 30 p.c. anthracene is raised to 90 p.c. (*v.* also Scholvien, Fr. Pat. 335013; J. Soc. Chem. Ind. 1904, 113).

The Aktien Gesellschaft fur Anilinfabrik (D. R. P. 178764; J Soc. Chem. Ind. 1907, 1193) add potassium hydroxide to the melted crude anthracene, which is then distilled *in vacuô*, the anthracene distilling over being passed into some solvent in which it is soluble at the temperature of the reaction, and from which it crystallises on cooling. It is stated that 95–96 p.c. of the anthracene is recovered as a product containing 95–98 p.c. of pure anthracene.

Wirth (Eng. Pat. 14462; J. Soc. Chem. Ind. 1901, 464) separates the carbazole by means of its easily soluble nitroso- compound. Crude anthracene is mixed in a vessel provided with a stirrer with light coal-tar oil and sodium nitrite. Dilute sulphuric acid is added gradually, and the sodium sulphate which is formed is dissolved in water and separated from the light-oil layer. The anthracene is filtered from the light coal-tar oil, washed with benzene, and dried. It contains 75–95 p.c. anthracene, according to quality of the crude material.

Catchpole (Eng. Pat. 16641; D. R. P. 164508; J. Soc. Chem. Ind. 1903, 1190) places the crude product in the form of blocks or slabs on a perforated or channelled surface in a chamber suitably heated to a temperature not exceeding 200°, whereby the impurities are 'sweated' out. A slight washing with acid and distillation complete the process.

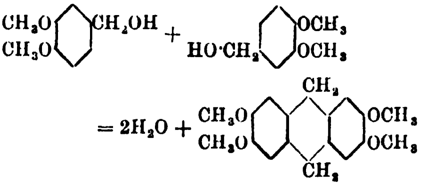
Vesely and Votocek (Eng. Pat. 27596; J. Soc. Chem. Ind. 1905, 191) find that concentrated sulphuric acid extracts the whole of the basic impurities of anthracene from a solution of crude anthracene in a solvent immiscible with sulphuric acid. The most suitable solvents are mineral and coal-tar oils, but carbon disulphide and chloroform may be used; 100 parts of crude anthracene (35 p.c.) are dissolved in 300 parts of solvent naphtha, 100 parts of concentrated sulphuric acid are added, and the mixture is heated and at the same time vigorously agitated for a few minutes. The sulphuric acid having been drawn off, the solution is freed from acid by agitation with calcium carbonate, filtered, and then allowed to crystallise. By this process it is stated to be possible to obtain an 85–90 p.c. anthracene, perfectly free from carbazole.

A troublesome impurity in anthracene is

a peculiar paraffin, which has a high melting-point, and is only sparingly soluble either in light petroleum or coal-tar naphtha; it is dissolved to a certain extent by these solvents when hot, but on cooling is almost entirely deposited again. A small quantity left in the anthracene frequently impedes succeeding operations, and, owing to its stability, passes through most of the processes without change.

Syntheses.—From orthotolylketone, by heating with zinc-dust (Behr and Van Dorp, Ber. 7, 17); from orthobromobenzylbromide, by the action of sodium (Jackson and White, Ber. 12, 1965); from a mixture of benzene, acetylene tetrabromide, and aluminium chloride (Anschütz, Annalen, 235, 156); from benzene and aluminium chloride under the influence of nickel carbonyl at 100° (Dewar and Jones, Chem. Soc. Trans. 1904, 213); and by treating pentachlorethane in benzene with aluminium chloride, when anthracene is formed through the intermediate formation of perchlorethylene (Mouneyrat, Bull. Soc. chim. 19, [3] 557). An interesting synthesis resulting in the production of methyl anthracene (m.p. 200°) is that of Kraemer and Spilker (Ber. 1890, 3174). By the interaction of xylene and cinnamene, phenyltolylpentane is formed, which when passed through a red-hot tube forms methyl anthracene (m.p. 207°), hydrogen and methane being evolved. This synthetical production of methyl anthracene is of importance in its relation to the present theories of the mode of formation of anthracene in coal tar.

The following syntheses in the anthracene group have been carried out in recent years. Mineral acids convert homopiperonyl and homoveratryl alcohols into derivatives of 2.3.6.7.-tetrahydroxy-9.10-dihydroanthracene



the tetramethoxy compound being obtained in quantitative yield by the condensation of veratrole with formaldehyde in the presence of 60 p.c. sulphuric acid (Robinson, Chem. Soc. Trans. 107, 267). Magnesium phenyl bromide reacts with ortho-phthalaldehydic acid in boiling anisole solution to produce ortho-*α*-benzhydrylbenzhydrol $HO{\cdot}CH(C_6H_5){\cdot}C_6H_4{\cdot}C(C_6H_5)_2{\cdot}OH$, and this, when boiled with hydrobromic acid, is converted into 9.10-diphenylanthracene (Simonis and Remmert, Ber. 48, 406). Purpurin (1.2.4-trihydroxyanthraquinone) may be synthesised by condensing phthalic anhydride with hydroxyquinol, whilst by using 4-hydroxy-phthalic anhydride, hydroxyflavopurpurin (1.2.4.6-tetrahydroxyanthraquinone), identical with the oxidation product of flavopurpurin, is obtained (Dimroth and Fick, Annalen, 411, 315).

Properties.—Anthracene crystallises in glistening white scales. It melts at 213°, and boils at 360° (Ullmann, Enzykl). When pure it shows a bluish-violet fluorescence, but this is concealed if small quantities of yellow impurities (Fritzsche's chrysogen) are present. Yellow-coloured anthracene, on exposure to sunlight, is bleached, and becomes fluorescent, but under these conditions the hydrocarbon undergoes conversion into paranthracene $(C_{14}H_{10})_2$—a peculiar modification, which is much less soluble than anthracene, is unattacked by bromine and nitric acid at 100°, and does not combine with picric acid; it melts at 244°, and is thereby converted into ordinary anthracene (Fritzsche, J. pr. Chem. 101, 333; Graebe and Liebermann, Annalen, Suppl. 7, 264; Schmidt, J. pr. Chem. [2] 9, 248). According to Luther and Weigert (Ch. Ztrbl. 1904, ii. 117; 1905, i. 1152), anthracene in the solid state, as well as in solution, yields para-anthracene. The fluorescence of anthracene and certain of its derivatives has been referred by Liebermann to a particular molecular grouping (Ber. 13, 913). Meyer (Zeitsch. physikal. Chem. 1897, 468) attributes fluorescence to the presence of what are known as fluorphoric groups, which must be situated between two heavy atomic groups, usually benzene nuclei. For a discussion of the cause of fluorescence in anthracene, *see* Stevenson (J. Physiol. Chem. 1911, 15, 845). The solubility of anthracene in 100 parts of various solvents has been determined by Versmann (Jahresbericht. 1874, 423), Perkin (Journ. Soc. Arts, 27, 598: v. Becchi, Ber. 12, 1978), Findlay (Chem. Soc. Trans. 1902, 1221) with the following results:—

			Parts of anthracene
Alcohol (absolute	at 16°	dissolves	0·076 (B.).
,, ,,	b.p.	,,	0·830 (B.).
,, sp.gr.=0·800	at 15°	,,	0·591 (V.).
,, ,, =-0·825	,,	,,	0·574 (V.).
,, ,, =0·830	,,	,,	0·491 (V.).
,, ,, =0·835	,,	,,	0·475 (V.).
,, ,, =0·840	,,	,,	0·460 (V.).
,, ,, =0·850	,,	,,	0·423 (V.).
Ether . .	,,	,,	1·175 (V.).
Chloroform .	,,	,,	1·736 (V.).
Carbon disulphide	,,	,,	1·478 (V.).
Acetic acid .	,,	,,	0·444 (V.).
Light petroleum	,,	,,	0·394 (V.).
,,	b.p. 70°–100° at 15°	dissolves	0·115 (P.).
Benzene . .	,,	,.	1·296 (F.).
,, b.p. 80°–100°	,,	,,	0·976 (P.).
Toluene . .	at 16·5°	,,	0·920 (B.).
,, . .	at b p.	.,	12·940 (B.).

According to Hildebrand, Ellefson, and Beebe (J. Amer. Chem. Soc. 1917, 39, 2301), the solubilities of anthracene at 25°, in grams per 100 grams of the solvents, are as follows:—

Alcohol	0·328
Benzene	1·86
Carbon disulphide . . .	2·58
Carbon tetrachloride . .	0·732
Ether ,, . .	1·42
Hexane ,, . .	0·37

When introduced into an alcoholic solution of picric acid saturated at 30°–40°, anthracene forms a picrate $C_{14}H_{10},C_6H_3(NO_2)_3O$, crystallising in glistening red needles which melt at 138°; it is decomposed into its constituents by alcohol, water, and dilute alkalis, even in the cold. The formation of the picrate is best obtained by warming molecular quantities of anthracene and picric acid on the water-bath in chloroform solution. On oxidation with potassium dichromate or manganese dioxide and sulphuric acid, anthracene is converted into anthraquinone, whilst strong nitric acid oxidises it to anthraquinone and dinitroanthraquinone; nitro- derivatives of anthracene can, however, be prepared by the action of strong nitric acid on the hydrocarbon, if care is taken to decompose any nitrous acid which may be formed during the reaction (Perkin, Chem. Soc. Proc. 1889, 13). Electrolytic oxidation in acetone yields anthraquinone (Fontana and Perkin, Chem. Zentr. 1904, ii. 708); the same product results by the electrolytic oxidation of a suspension of anthracene in a 2 p.c. solution of cerium sulphate in 20 p.c. sulphuric acid at 80°-90° (Farb. vorm. Meister, Lucius, and Brüning, D. R. P. 152063; Chem. Zentr. 1904, ii. 71); or by the oxidation of anthracene by cerium oxide in sulphuric acid (Farb. M. L. & B.; D. R. P. 158609; Chem. Zentr. 1905, i. 840); or by heating anthracene with charcoal at 150°-300° (Dennstedt and Hassler, D. R. P. 203848; Chem. Zentr. 1908, ii. 1750).

Concentrated sulphuric acid converts anthracene into sulphonic acids. Anthracene monosulphonic acid is obtained by the direct sulphonation of anthracene with sulphuric acid of 53° or 54°B., and about 60 p.c. of the anthracene employed is thus converted. If sulphuric acid of 66°B. is used, two isomeric disulphonic acids are obtained, and these, on oxidation, yield two anthraquinonedisulphonic acids, which are isomeric with the two acids obtained by the direct sulphonation of anthraquinone. The *β*-anthracene disulphonic acid, after oxidation with chromic or nitric acids, and subsequent fusion with alkali, yields *alizarin* (*q.v.*), and the monosulphonic acid similarly treated yields *anthrapurpurin* (*q.v.*) (La Société Anonomye des Matières Colorantes et Produits Chemiques de St. Denis, Eng. Pat. 1280; J. Soc. Chem. Ind. 1894, 32).

The same acids are obtained by heating anthracene with alkali bisulphate to 140°-150° (D. R. P. 77311). Anthracene is readily attacked by chlorine and bromine, and yields with each element a series of additive and substitution derivatives; additive compounds, apparently, are the first products of the action, and these either decompose during the reaction or can be decomposed by boiling with alcoholic potash into the corresponding substitution derivatives, which also form additive compounds by the further action of the halogens. The chloranthracenes are now prepared on a large scale (Clayton Aniline Co., Eng. Pat. 8744; J. Soc. Chem. Ind. 1906, 64). Dry chlorine reacts with anthracene in the presence of lead peroxide at a high temperature. Fifty parts by weight of anthracene and 10 parts of dry powdered lead peroxide are treated with dry chlorine at 220° until the weight has increased to 120 parts. The temperature, however, may be varied between 180° and 260°, and the composition of the product varies with the temperature employed and the amount of chlorine absorbed. The product consists mainly of *β*-tetrachloranthracene (m.p. 152°), which is readily soluble in benzene and crystallises out in yellow needles, and another part much less soluble in benzene and more highly chlorinated. This latter consists of two products: hexachloranthracene (m.p. 277°), which crystallises from nitrobenzene, and heptachloranthracene (m.p. 232°), which is more soluble in benzene than the former. Oxidation converts these compounds into chloranthraquinones, containing 2 atoms of chlorine less than the original compound. Treatment with a mixture of nitric and sulphuric acids results in the formation of chlornitroanthraquinones which yield dyestuffs on treatment with fuming sulphuric acid. The chloranthraquinones on treatment with fuming sulphuric acid in the presence or absence of boric acid, yield hydroxy- compounds; *e.g.* 1:4 dichloranthraquinone yields *quinizarin* (*q.v.*) (Farb. vorm. F. Baeyer & Co., Fr. Pat. 385358; J. Soc. Chem. Ind. 1908, 557). Reducing agents, such as sodium amalgam or phosphorus and hydrogen iodide, convert anthracene into the dihydride (Graebe and Liebermann, *l.c.*; Liebermann and Topf., Annalen, 212, 5); hydrogen and nickel oxide at 260°-270° and 100-125 atmos. convert anthracene first into tetrahydro-, then decahydro-, and finally perhydroanthracene (Ipatieff, Jokowleff, and Rakitin, Ber. 1908, 996).

Estimation.—Luck (Ber. 6, 1347); Meister, Lucius, and Bruning (Dingl. polv. J. 224, 559); Nicol (Chem. Soc. Trans. 1876, 2, 553); Bassett (Chem. News, 73, 178; 79, 157). The percentage of anthracene in a sample of the commercial product is determined by oxidising it to anthraquinone with chromic acid, dissolving the product in sulphuric acid, and precipitating with water, since the associated impurities are either destroyed during the oxidation or are converted into sulphonic acids soluble in water. The details of the process are as follows: 1 gram of anthracene is introduced with 45 c.c. of acetic acid into a flask connected with a reversed condenser, and heated to boiling; a solution of 15 grams of chromic acid in 10 c.c. of acetic acid and 10 c.c. of water is then added, drop by drop, to the boiling solution during a period of 2 hours; and the product is boiled for 2 hours longer, allowed to stand for 12 hours, then poured into 400 c.c. of water, and, after standing for 3 hours longer, is filtered. The anthraquinone on the filter is washed with water, with hot dilute alkali, and then with hot water; afterwards it is placed in a small dish dried at 100°, and digested for 10 minutes with 10 times its weight of pure concentrated sulphuric acid at 100°. The solution of anthraquinone in sulphuric acid is then allowed to remain for 12 hours in a moist atmosphere, mixed with 200 c.c. of water, and the precipitated anthraquinone filtered off and washed first with water, then with dilute alkali, and finally with water; it is then dried at 100° in a dish, weighed, ignited, and the ash deducted from the first weighing. The difference gives the weight of anthraquinone corresponding to the amount of anthracene present in the sample.

Impurities.—Paraffin is usually present in crude anthracene, and is estimated by treating the material with fuming nitric acid, keeping the mass cold. When all the acid has been added, the mixture is kept at the ordinary temperature until the anthracene has dissolved, and then heated until the paraffin has melted. The solution is filtered and the precipitate washed with fuming nitric acid until the filtrate dissolves in water without turbidity, and then with water until neutral. Finally, the paraffin is washed with alcohol, dissolved in warm ether and the filtrates collected in a weighed porcelain dish; the filtrates are evaporated and the paraffin dried at 105°–110° for half an hour (Heusler and Herde, J. Soc. Chem. Ind. 1895, 828). Kraemer and Spilker (Muspratt-Bunte, vii. 70) use the following method: 10 grams finely-powdered anthracene are shaken with 100 c.c. ether for ten minutes and mixture then allowed to settle. 50 c.c. of the clear solution are then evaporated and the residue dried at 100° for half an hour. After cooling, the residue is finely ground, 8 c.c. fuming sulphuric acid (20 p.c. SO_3) added, well mixed, and the whole heated to 100° for three hours, with frequent stirring. Contents of dish are then washed by means of 500 c.c. hot water into a beaker, filtered through a dry filter and the whole washed with cold water, until filtrate is free from sulphuric acid. Moisten filter with absolute alcohol and wash the paraffin into a weighed dish by means of ether, removing last traces of paraffin from the beaker in the same manner. Evaporate ether solutions and dry residue for half an hour at 105°; and weigh as pure paraffin The detection of carbazole and phenanthrene in the purified product is carried out as follows:—

Carbazole. Sample is extracted in cold with ethyl acetate, solution allowed to evaporate, and residue transferred by a few drops of same solvent to a watch-glass. On evaporation, carbazole is left behind; when treated with a drop of nitrobenzene and phenanthraquinone, it yields characteristic small copper-coloured plates.

Phenanthrene. Sample is extracted with benzene, and the evaporation residue treated with α-dinitrophenanthraquinone in nitrobenzene. In this case mixed crystals are obtained having the form and colour of the brown needles of the phenanthrene compound, but containing a large quantity of anthracene.

ANTHRACENE ACID BROWN, -CHROME BLACK, -RED, -YELLOW *v.* AZO- COLOURING MATTERS.

ANTHRACENE GREEN. *Cœruleïn* and *Cœruleïn S.* (*v.* ALIZARIN AND ALLIED COLOURING MATTERS; also XANTHINE COLOURING MATTERS).

ANTHRACENE VIOLET. *Galleïn* (*v.* ALIZARIN AND ALLIED COLOURING MATTERS; also XANTHINE COLOURING MATTERS).

ANTHRACHRYSONE *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHRACITE *v.* FUEL.

ANTHRACITE BLACK *v.* AZO- COLOURING MATTERS.

ANTHRACOXENE *v.* RESINS.

ANTHRACYL CHROME GREEN *v.* AZO-COLOURING MATTERS.

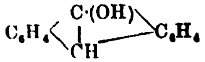
ANTHRAFLAVIC ACID *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHRAGALLOL *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHRAGALLOL DIMETHYL ETHERS *v.* CHAY ROOT.

ANTHRANIL, ANTHRANILIC ACID (*o-aminobenzoic acid*) *v.* AMINOBENZOIC ACID AND

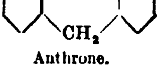
ANTHRANOL. 9-*Hydroxyanthracene*



$$C_6H_4\left\langle\begin{matrix}C\cdot(OH)\\ |\\ CH\end{matrix}\right\rangle C_6H_4$$

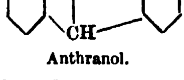
is prepared by the reduction of anthraquinone with hydriodic acid and phosphorus (Liebermann and Topf, Annalen, 212, 6; Ber. 1876, 1201), or with tin and acetic acid (Liebermann and Gimbel, Ber. 1887, 1854). Another method is to add copper or aluminium powder to anthraquinone dissolved in concentrated sulphuric acid at 30°–40°, and pour the product into water. The crude substance is recrystallised from glacial acetic acid containing a trace of aluminium and a little hydrochloric acid (Baeyer & Co. D. R. P. 201542: Chem. Zentr 1908, ii. 1218, Bezdizk and Friedlander, Monatsh. 30, 871). It is also obtained when 50 parts of finely divided anthraquinone are mixed with 10 parts of iron and 1000 parts ferrous chloride, and the mixture heated to 200° C. or higher, until it dissolves in sodium hydroxide solution with a yellow colour. The product is then cooled and washed with water, the residue dissolved in sodium hydroxide solution, and filtered into hydrochloric acid (D. R. P. 249124). Anthranol has been synthesised by heating 1 part of *o*-benzylbenzoic acid with 2 parts of sulphuric acid at 100° (Fischer and Schmidt, Ber. 1894, 2789). It crystallises in colourless needles, m.p. 165°, with decomposition. It dissolves in alkalis, and then behaves as its tautomeride anthrol (*q.v.*); *e.g.* it condenses with benzaldehyde to form benzilidine anthrol (Haller and Padova, Compt. rend. 141, 857; *v.* also Bad. Anil. und Soda Fab. D. R. P. 172930; Chem. Zentr. 1906, ii. 834). By heating the alkaline solution of anthranol for some time, it becomes oxidised to anthraquinone; hydroxylamine hydrochloride converts it into anthraquinonedioxime (Nietzki and Kehrmann, Ber. 1887, 613). Anthranol yields a benzoyl derivative (m.p. 164°) with benzoyl chloride in pyridine (Padova, Compt. rend. 143, 121; Ann. Chim. Phys. [8] 19, 353), and a diiodide with iodine in benzene solution (Liebermann, Glawe, and Lindenbaum, Ber. 1904, 3337)

Kurt Meyer (Annalen, 1911, 379, 37) has obtained the two desmotropic forms of anthranol, namely, anthrone and anthranol:



Anthrone.

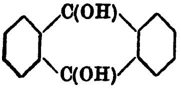
and



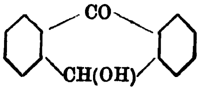
Anthranol.

The keto-form is prepared by reducing anthraquinone with tin and hydrochloric acid, and subsequent precipitation with water. It melts at 154°, and is almost completely insoluble in cold alkali solutions. On solution in boiling dilute sodium hydroxide, rapid cooling and precipitation with dilute well-cooled sulphuric acid, the yellow anthranol is obtained. It melts at about 152°, dissolves readily in most solvents, being converted into anthrone. Solutions of anthranol show a strong fluorescence, those of anthrone no fluorescence. Thiele's assumption that the high reactivity of phenols is due to a change to the keto-type seems to be contradicted here, for in the above pair of compounds the hydroxylic form is the more active isomeride.

Bromo-anthrone is obtained when bromine is added to a cold saturated solution of anthrone in CS_2. It crystallises in yellow needles, and melts at 148°. On boiling with aqueous acetone it yields oxanthrone, which crystallises in colourless needles, melting at 167°. Solutions of oxanthrone are colourless and do not fluoresce. On boiling with aqueous alkali it passes into the desmotropic form anthraquinol, which is also formed when anthraquinone is reduced by zinc-dust and alkali. It crystallises in brown leaflets, which dissolve in solvents with a yellow colour and an intense green fluorescence.



Anthraquinol.



Oxanthrone.

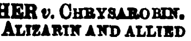
By the oxidation of anthracene in glacial acetic acid solution with lead peroxide (1 mol. $C_{14}H_{10}$; 1 mol. PbO_2) anthranol acetate is produced, but if in the proportions of 1 mol. $C_{14}H_{10}$; 2 mols. PbO_2, then oxanthrone acetate results. The former melts at 127°, and is readily hydrolysed to anthranol, the latter melts at 108°–109°. Again, by dissolving anthracene in glacial acetic acid, pouring into water and passing chlorine, oxanthrone is obtained in about 75 p.c. yield (K. Meyer, *l.c.*). Oxanthrone is also obtained by the following method (D. R. P. 250075), 3·4 parts of anthracene are dissolved in 200 parts acetone, and then precipitated by the addition of 200 parts ice-cold water. 6·4 parts of bromine are added, with continual shaking, all goes into solution, much cold water is added, and the oxanthrone is precipitated. It crystallises from toluene in long yellowish needles.

Dianthranol $C_{28}H_{18}O_2$ is formed, together with a little anthraquinone, when anthranol dissolved in benzene is exposed to sunlight for some weeks, or when the benzene solution is boiled for some hours. It is also obtained by oxidising anthranol with ferric chloride, in glacial acetic acid solution, or (D. R. P. 223209) by heating 100 parts anthraquinone, 500 parts of water, 50 parts sodium hydroxide, and 50 parts zinc-dust in an autoclave for six hours at 160° C. The reaction mixture is then precipitated by the addition of acid, and recrystallised from methyl alcohol. On oxidation with potassium permanganate it yields dianthrone $C_{28}H_{16}O_2$, a yellow crystalline solid which blackens at 300° C. Dianthranol crystallises in colourless tabular crystals (m.p. 250°) (Orndorff and Bliss, Amer. Chem. J. 1896, 453; Orndorff and Cameron, Amer. Chem. J. 1895, 658).

ANTHRANOLS of **CHRYSOPHANIC ACID** and **EMODIN METHYL ETHER** *v.* CHRYSAROBIN.

ANTHRAPURPURIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHRAQUINONE



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4.$$

Obtained by the oxidation of anthracene with chromic acid (Kopp, Jahresbericht. 1878, 1188; Laurent, Ann. Chim. Phys. [2] 60, 220; 72, 415; Annalen, 34, 287; Anderson, Annalen, 122, 301; Graebe and Liebermann, Annalen, Spl. 7, 285); by the distillation of calcium benzoate (Kekulé and Franchimont, Ber. 1872, 908); by the distillation of benzoic acid with phosphorus pentoxide; by the distillation of *o*-benzoylbenzoic acid with phosphorus pentoxide, or by heating it alone (Ullmann, Annalen, 291, 24; Behr and Dorp, Ber. 1874, 578; Liebermann, Ber. 1874, 805; Perkin, Chem. Soc. Trans. 1891, 1012); by the dry distillation of calcium phthalate (Panaotovits, Ber. 1884, 13). Heller (Zeitsch. angew. Chem. 1906, 19, 669) heats 1 part of phthalic anhydride with 3·5 parts of benzene and 1·8 parts of aluminium chloride in a lead vessel at 70° until the evolution of hydrogen chloride ceases. After cooling, water is added and the excess of benzene removed by steam distillation. The solution is made alkaline and boiled, and then on addition of acid benzoyl benzoic acid is precipitated. On heating this for one hour at 150°, anthraquinone is obtained (*cf.* Piccard, Ber. 1874, 1785; Friedel and Crafts, Ann. Chim. Phys. [6] 1, 523; Müller, J. 1863, 393). Phenyl-*o*-tolylketone gives anthraquinone on heating with lead oxide or on oxidation with manganese dioxide and sulphuric acid (Behr and Dorp, Ber. 1873, 754; 1874, 16; Thörner and Zincke, Ber. 1877, 1479).

Industrial preparation.—Crude anthracene (55-60 p.c.) is slowly added to a hot solution of sodium dichromate in a large wood vat lined with lead. The solution is kept well stirred and heated with steam until all the anthracene has been added. The steam is then cut off and sulphuric acid is run into the mixture in the form of a fine spray; the heat generated by the reaction keeps the solution boiling. The crude anthraquinone is then separated by filtration and dried. It is dissolved in sulphuric acid without applying any heat, and, when solution is complete, transferred to a large vat lined with lead and boiled with water. The precipitated anthraquinone is at once separated by means of filter presses from the soluble compounds; the pressed cakes are boiled with a solution of soda, and then again filtered, pressed, dried, and finally sublimed (Levinstein, J. Soc. Chem. Ind. 1883, 219; Kopp, *l.c.*). Poirrier and Rosenstiehl (Eng. Pat. 8431; J. Soc. Chem. Ind. 1887, 595) oxidise anthracene in a closed lead-lined vessel by means of ferric sulphate. The vessel is heated to 120°–150° during 72 hours, compressed air being injected into the vessel. By this means the anthracene is virtually oxidised by the air, the ferric sulphate acting as a carrier for oxygen. The Farbenfabrik vorm. Meister, Lucius und Brüning, state that an almost quantitative yield of anthraquinone is obtained by the electrolytic oxidation of anthracene in 20 p.c. sulphuric acid, in the presence of cerium sulphate (D. R. P. 152063; Eng. Pat. 19178, 1902). Another process consists in the absorption of nitric oxides diluted with air, by zinc oxide, copper oxide, or a similar oxide of low basicity. Anthracene is mixed with this, and a stream of air or oxygen is passed through the mixture at 250°–350°, anthraquinone being produced (Ch. Fabr. Grünau, Landshoff und Meyer, D. R. PP. 207170, 215335; J. Soc. Chem. Ind. 1909, 360, 1310). On the use of oxides of nitrogen and nitric acid for oxidising anthracene, *see* D. R. PP. 234289, 254710, 256623. Meister, Lucius, and Brüning (D. R. P. 292681) make a mixture of 100 parts 30 p.c.

aqueous anthracene paste, with 3000 parts water, 250 parts 25 p.c. ammonia, and 5 parts copper oxide. Oxygen corresponding to 3 molecules per molecule of anthracene is forced in and the whole stirred and heated for two hours at 170° C. Darmstädter (Chem. Zentr. 1900, ii. 151; D. R. P. 109012) prepares anthraquinone by the electrolytic oxidation of anthracene in a chromic-acid bath. Various processes have been patented for purifying the crude anthraquinone thus produced. Bronner (J. Soc. Chem. Ind. 1882, 499; 1883, 410; Eng. Pat. 759; D. R. P. 21681) dissolves out the impurities on a specially constructed circular shelf. The method depends on the continuous extraction of the impure product with an amount of solvent insufficient to keep in solution the whole of the anthraquinone and the easily soluble impurities. Bayer & Co. (D. R. P. 68474; Eng. Pat. 5539; J. Soc. Chem. Ind. 1893, 439) dissolve out the impurities with liquid sulphur dioxide; Sadler & Co., Ltd. and Driedger (Eng. Pat. 17635; J. Soc. Chem. Ind. 1902, 1072) recrystallise the crude anthraquinone from hot aniline. The chromium liquors may be recovered and used again, by a process of electrolytic oxidation in iron cells which are lined with lead. Strips of lead, hanging in the cells, act as cathodes, and the liquor is circulated through a series of cells.

Properties.—Anthraquinone, as usually prepared, forms a felted mass of crystals of a pale-yellow or buff colour; by sublimation it can be obtained in the form of lemon-yellow needles or golden-yellow prisms; m.p. 285°-286° (corr.); b.p. 379°-381° (corr.) (Recklinghausen, Ber. 1893, 1515); sp.gr. 1·438-1·419 (Schroeder, *ibid.* 1880, 1071; Phillipi, Monatsh. 1912, 33, 373). Sparingly soluble in alcohol and ether, somewhat more soluble in hot benzene. According to Hildebrand, Ellefson, and Beebe (J. Amer. Chem. Soc. 1917, 39, 2301), the solubilities of anthraquinone at 25°, in grams per 100 grams of the solvents, are as follows:—

Alcohol	0·437
Ether	0·104

It is neutral in its reactions, and is insoluble in dilute acids or alkalis. Anthraquinone is very stable; it is not affected by hot hydrochloric acid, or by boiling with caustic potash or calcium hydroxide solutions; it dissolves in hot nitric acid (sp.gr. 1·4), and is deposited in crystals on cooling or on dilution; it dissolves unchanged in concentrated sulphuric acid at 100°, and is precipitated in fine crystals on pouring into water. Strongly heated with sulphuric acid, it is converted into mono- and di-sulphonic acids (*v.* ALIZARIN). Anthraquinone is of great commercial importance, as it is used in the preparation of alizarin, quinizarin, purpurin, &c. (*v.* ALIZARIN). Fusion with zinc or treatment with sodium methoxide converts it into anthracene (Haller and Minguin, Compt. rend. 120, 1105); fusion with caustic soda converts it into sodium benzoate (Graebe and Liebermann, Annalen, 160, 129), and by distilling it over lime benzene is formed; reduction with zinc and caustic soda, or with sodium amalgam yields oxanthranol $C_{14}H_{10}O_2$ and dianthranol (Diels and Rhodius, Ber. 1909, 1076; Meyer, Ber. 1909, 143); zinc and amyl alcohol convert it into dianthrol (Meyer, Monatsh. 30, 165). Phosphorus pentachloride and phosphorus oxychloride convert it into trichloranthracene and other chlorinated products (Radulescu, Chem. Zentr. 1908, ii. 1032). A delicate test for anthraquinone consists in reducing it with sodium amalgam in dry ether. On adding a drop of water, a red colouration is produced; if alcohol is used instead of ether, addition of water gives a green colouration (Claus, Ber. 1877, 927).

The following method serves to estimate anthraquinone in presence of anthracene, and not more than 10 p.c. of phenanthraquinone, with an error not exceeding 0·3 p.c. One part of the crude anthraquinone is wetted with alcohol, mixed with 2 parts of zinc-dust, and about 50 parts of hot 5 p.c. sodium hydroxide solution. The mixture is heated just below boiling-point for five minutes, and then rapidly filtered and washed once with water. The filter with the residue is heated with another equal portion of sodium hydroxide solution and filtered into the same flask. The residue is again treated with sodium hydroxide solution, and if it imparts no red colour to this on boiling, is rejected. Otherwise the liquid is filtered off, and the residue treated with sodium hydroxide repeatedly until anthraquinone is shown to be completely reduced to oxanthranol and removed, by the failure of the residue to impart a red colour to boiling sodium hydroxide solution. The united filtrates are cooled and reoxidised by shaking until the red colour disappears. The anthraquinone is filtered off on asbestos, dried at 110°, and weighed. The following precautions are necessary: Boiling with alkali must not be unduly prolonged, or reduction may proceed so far that anthraquinone is not reconstituted on mere shaking with air, and filtration of the reduced solution must be rapid to prevent reoxidation on the filter (Lewis, J. Ind. and Eng. Chem. 1918, 10, 425; Analyst, 1918, 297).

Condensation products.—With phenols: Scharwin and Kusnezof, Ber. 1903, 2020; 1904, 3616; Deichler, D. R. P. 109344; Chem. Zentr. 1900, ii. 360. With amines: Bayer & Co. D. R. PP. 86150, 107730, 136777, 136788, 148079; Chem. Zentr. 1902, ii. 1272; Chem. Soc. Abst. 1904, i. 326. Aryl ethers, aryl- and alkylamino- derivatives: Bayer & Co. D. R. P. 158531; Fr. Pats. 354717, 362140; J. Soc. Chem. Ind. 1905, 885, 1105; 1906, 752. Thiocyanates: Bayer & Co. D. R. P. 206054; J. Soc. Chem. Ind. 1909, 239. Mercaptans: *ibid.* 469.

A cooled solution of anthraquinone in concentrated sulphuric acid, when treated with aluminium powder with constant stirring, yields anthraquinol and anthrone.

1.2- and 1.4-anthraquinones have been prepared from α-anthrol and 1.2-anthraquinone from β-anthrol (*v.* Dienel, Ber. 1906, 926; Liebermann, Ber. 1906, 2089; Harlinger, Ber. 1906, 3537; Lagodzinski, Ber. 1894, 1483; 1895, 1422; 1906, 1717).

ANTHRAQUINONE RED *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

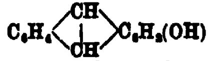
ANTHRAQUINONE SULPHONIC ACIDS *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHRAROBIN *v.* CHRYSAROBIN.

ANTHRARUFIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHRASOL. A trade name for a preparation of coal-tar with the colour and consistence of olive oil.

ANTHROL



$$C_6H_4\begin{matrix}CH\\|\\CH\end{matrix}C_6H_3(OH)$$

Two isomeric anthrols are known, α- or 1-hydroxyanthracene and β- or 2-hydroxyanthracene.

α-Anthrol is prepared by fusing 1-anthracenesulphonic acid with 5 parts of caustic potash at 250°, dissolving the mass in water, and filtering off the yellow flocks which separate out. The crude product is recrystallised from acetic acid and water. It forms yellow plates, m.p. 152°. α-Anthrol dissolves in the ordinary solvents with a blue fluorescence, and is more soluble than β-anthrol (Schmidt, Ber. 1904, 66; Dienel, Ber. 1905, 2862; *v.* also Linke, J. pr. Chem. [2] 11, 227). It is used in the preparation of alizarin-indigo G, which is obtained from dibromo-isatin chloride and α-anthrol (D. R. P. 237199).

β-Anthrol is prepared by fusing 2-anthracenesulphonic acid with potash and recrystallising the crude product from acetone (Liebermann and Hörmann, Ber. 1879, 589; Linke, J. pr. Chem. [2] 11, 222). It can also be obtained by reducing hydroxyanthraquinone with hydriodic acid and phosphorus (Liebermann and Simon, Ber. 1881, 123). It forms yellow plates melting with decomposition at 200°, and is soluble in the common organic solvents with a violet fluorescence. By reduction with sodium in alcoholic solution, dihydroanthrol is obtained (Bamberger and Hoffmann, Ber 1893, 3069), and by heating with acetamide at 280° *anthramin* is obtained. Azo- dyestuffs have been obtained from β-anthrol (Act. Ges. f. Anilinf. D. R. P. 21178; Frdl. i. 538) It possesses a somewhat phenolic character, but more resembles the naphthols in that on heating with ammonia to 200° C. it yields the corresponding anthramine. If, however, it be reduced to the dihydroanthrol, this is the complete analogue of phenol, and does not condense with ammonia to the amine.

ANTIAR RESIN or **UPAS ANTIAR.** A green resin which exudes from the upas tree (*Antiaris toxicaria* (Lesch.), order Maraceæ). Light petroleum and benzene extract from it a substance analogous to caoutchouc, a fatty matter, and two resinous substances; alcohol extracts from the residue a very poisonous glucoside, *antiarin* (De Vrij and Ludwig, J. pr. Chem. 103, 253).

ANTIARIN *v.* DIGITALIS; GLUCOSIDES.

ANTIARTHRIN. A trade name for a condensation product of saligenin and tannin.

ANTI-CHLOR. Linen and cotton fibres and paper pulp are apt to retain some free chlorine from the hypochlorite used in bleaching, and as this causes the material to rot slowly, the manufacturers use certain reagents known as 'anti-chlors' to remove the last traces of chlorine. The first substances employed were the neutral and acid sulphites of soda (sodium sulphite and bisulphite); these were superseded in 1853 by sodium hyposulphite, which is now very largely employed. Calcium sulphide, made by boiling milk of lime with sulphur; stannous chloride in hydrochloric acid with subsequent treatment with sodium carbonate to neutralise any free acid; ammonia and sodium nitrite have also been recommended.

ANTIDIABETINE. Trade name for a preparation said to be composed of saccharin and mannite.

ANTIDIN. Phenyl ether of glycerol

ANTI-FEBRIN. A trade name for *acetanilide* or *phenylacetamide* $C_6H_5{\cdot}NH{\cdot}CO{\cdot}CH_3$. Discovered by Gerhardt in 1853, and investigated as an antipyretic by Kussmaul in 1886 (*v.* ACETANILIDE).

ANTIFORMIN. Trade name for the alkaline liquid prepared by adding caustic soda to a solution of sodium hypochlorite. Used as a disinfectant, the active ingredient being the chlorine, of which 4 p.c. is liberated on treatment with hydrochloric acid. Solutions of sodium hypochlorite are prepared in Germany by the electrolysis of 5 p.c. salt solution. A current of 110 volts and 100 amperes furnishes nearly 6000 litres daily of a disinfecting or bleaching solution containing 1 p.c. of available chlorine.

According to H. Will (Zeitsch. Ges. Brauw. 1903, 865; J. Soc. Chem Ind. 1904, 125), it is one of the best disinfectants for brewery work It rapidly softens organic impurities and facilitates their removal by scouring, in addition to its oxidising action, and it also dissolves incrustation. Its germicidal power is high, and a 5 p.c. solution is sufficient for most purposes. It is used cold, and may be safely applied to varnished surfaces with a brush, provided care is taken to prevent prolonged contact.

ANTIFUNGIN. Trade name for magnesium borate, employed as a fungicide.

ANTIGERMIN. Trade name for a preparation of a copper salt of a phenol-carboxylic acid mixed with lime. It is used as a fungicide.

ANTIHYPO. A solution of potassium percarbonate, used for destroying sodium thiosulphate in photographic negatives and prints.

ANTILEPROL. Syn. for chaulmoogra oil as used in pharmacy.

ANTILUETIN. Potassium-ammonium antimonyltartrate.

ANTIMONIALS, ORGANIC.

Historical. The first organic derivative of antimony was synthesised by Löwig and Schweitzer, who prepared triethylstibine in 1850 (Mitth. d. Züroh. Naturforsch. Gesellschaft. 1850, 45, 1; Annalen, 1850, 75, 315, 327).

This synthesis was immediately extended by H. Landolt (Annalen, 1851, 78, 91), and further investigations of aliphatic antimonials were made by Hofman (1857) and by Buckton (1860). The first aromatic antimonials were prepared about 30 years later by Michaelis, who, in collaboration with Reese, Hasenbäumer and others, developed a general method for the synthesis of antimony derivatives containing one, two, or three acyl groups.

In 1910 these researches were revised by Morgan and Micklethwait (Chem. Soc. Trans. 1911, 99, 2293), who showed that triphenylstibine on heating with antimony chloride yields both mono- and diphenylstibine chlorides, and who determined the effect of the antimony complex on the orientation of a nitro group. Similar investigations were made independently by P. May, who also studied the reduction of the nitrated arylantimony compounds and arrived at concordant results (Chem. Soc. Trans. 1912, 101, 1033).

The diazo synthesis of aryl antimony compounds was first employed by the Chemische Fabrik von Heyden of Dresden, and this led to the synthesis of antimony atoxyl and antimony salvarsan (Fabr. Heyden. D. R. P. 254421)

Syntheses of aliphatic antimonials are few compared with those in the arsenic series, and are attended by greater experimental difficulties Syntheses are successful only when the more energetic reagents are employed, owing to the feebler affinity of antimony for hydrocarbon radicals.

Antimony analogues of certain of the therapeutic organic arsenicals have been prepared, but although when tested therapeutically they show trypanocidal power, and sometimes confer immunity to trypanosomes, yet so far nothing comparable with the specific action of aromatic arsenicals has been observed. Local irritation has been found to accompany subcutaneous introduction, but possibly this disagreeable effect might be overcome by intravenous injection

Stibacetin, the antimonial analogue of arsacetin, has been tried successfully in rendering mice immune against various strains of trypanosomes, the immunising dose being one-tenth of the lethal proportion. Uhlenhuth has reported on the effect of this drug on the growth of experimental tumours in rats and mice (Medizinische Klinik, 1912, 37) Sulphoform (triphenylstibine sulphide) has been employed medicinally as a remedy in skin diseases.

SYNTHESES OF ALIPHATIC ANTIMONIALS.

I. Interaction of an Alkyl Halide with an Alloy of Antimony.

Ethyl iodide, chloride or bromide reacts with an alloy of potassium and antimony (12 p.c. potassium), yielding triethylstibine and tetraethylstibonium halide. These products are not accompanied by any antimonial analogue of ethylcacodyl.

II. Interaction of an Alkyl Halide with Antimony.

Methyl iodide heated with antimony in a sealed tube at 140° yields *trimethylstibine diiodide* $Sb(CH_3)_3I_2$ (Buckton, Journ. Chem. Soc 1860, 13, 120; Jahresber, 1860, 374)

III. Interaction of a Metallic Alkyl with an Antimony Halide.

Zinc dimethyl reacts with antimony trichloride, giving trimethylstibine (Hofmann, Jahresber. 1857, 103, 357).

The Grignard reaction may also be employed. Antimony trichloride treated with Grignard reagent (*magnesium methyl iodide*) gives a 60-70 p.c. yield of trimethylstibine (Hibbert, Ber., 1906, 39, 160).

ALIPHATIC ANTIMONIALS.

Trimethylstibine $Sb(CH_3)_3$. Synthesised by method I. (above), and is ordinarily prepared in the same manner.

Colourless liquid, b.p. 80·6°, D 1·523/15°; odour of onions, soluble in ether, slightly soluble in water or alcohol; spontaneously inflammable in air or chlorine (Landolt, Annalen, 1851, 78, 91; Jahresber. 1861, 569).

The *dichloride* $Sb(CH_3)_3Cl_2$, and the corresponding *dibromide* are produced by direct addition of the halogen.

Tetramethylstibonium iodide $Sb(CH_3)_4I$ Formed by direct combination of trimethylstibine and methyl iodide Hexagonal plates, very soluble in water or alcohol, less so in ether; bitter saline taste

Tetramethylstibonium hydroxide, deliquescent crystalline mass obtained by treating the iodide with moist silver oxide; resembles caustic potash; its salts are crystalline and devoid of emetic action.

Triethylstibine $Sb(C_2H_5)_3$. Synthesised by method I (above), and ordinarily prepared in the same manner or by method III. (above) Colourless liquid, b p 158 5/730 mm. D 1 3244/16°, odour of onions, soluble in ether or alcohol, insoluble in water, spontaneously inflammable (Lowig and Schweitzer, Annalen, 1850, 75, 315; Hofmann, Annalen, 1857, 103, 357, Buckton, Quart. J. Chem. Soc, 1863, 13, 116, 118).

Tetraethylstibonium iodide $Sb(C_2H_5)_4I,1\frac{1}{2}H_2O$. Hexagonal prisms, fairly soluble in water, more so in alcohol and less so in ether.

Tetraethylstibonium hydroxide, prepared from the iodide and moist silver oxide, is oily, miscible with water or alcohol, and forms crystalline but hygroscopic salts.

Triamyl stibine $Sb(C_5H_{11})_3$, prepared by method I. (above). Fuming liquid heavier than water, oxidising to *triamylstibine oxide*

$$Sb(C_5H_{11})_3O$$

SYNTHESES OF AROMATIC ANTIMONIALS.

I. Interaction of sodium with chlorobenzene and antimony trichloride in benzene solution.

The mixture heated for 24 hours yields triphenylstibine, triphenylstibine dichloride and diphenylstibine trichloride. Triphenylstibine heated under pressure with antimony trichloride gives phenylstibine dichloride and diphenylstibine chloride, the sodium condensation thus leading from tertiary to primary and secondary antimonials

II. Grignard reaction. Antimony trichloride heated with magnesium aryl bromide or iodide gives triarylstibine as chief product, but the diaryl and monaryl antimony compounds may be obtained from the tertiary stibine by heating with antimony trichloride (Morgan and Micklethwait, *l.c*, *cf* Pfeiffer, Ber 1904, 37, 4621)

III. **Diazo-synthesis.** This method was discovered by the Chemische Fabrik von Heyden, who in 1911 showed that the stibinic group could by this means be introduced into aromatic nuclei *Phenylstibinic acid* is prepared by diazotising aniline, which is then treated with a cooled solution of antimony trichloride in aqueous sodium hydroxide. After some hours the mixture is almost neutralised with dilute sulphuric acid, and the phenylstibinic acid is precipitated from the filtered solution by hydrochloric acid. As thus prepared, phenylstibinic acid differs appreciably from specimens obtained *viâ* phenylstibinic chloride, showing decided tendency to form salts with ammonia and sodium hydroxide.

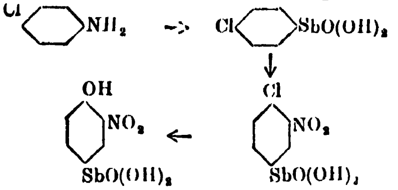
p-*Hydroxyphenylstibinic Acid*

$HO{\cdot}C_6H_4{\cdot}SbO(OH)_2$

and p-*Aminophenylstibinic Acid* (p-*Stibanilic Acid*) $NH_2{\cdot}C_6H_4{\cdot}SbO(OH)_2$ are both prepared by analogous methods. The sodium salt of the latter is the antimonial analogue of atoxyl (*q.v.*), and has similar therapeutic properties. Acetyl-*p*-phenylenediamine is diazotised and converted into acetyl-*p*-aminophenylstibinic acid by treatment with alkaline solution of antimony trichloride. The product is hydrolysed into *p*-aminophenylstibinic acid.

The sodium salt of acetyl-*p*-aminophenylstibinic acid is 'stibacetin,' the antimony analogue of 'arsacetin.'

When acetyl-*p*-aminophenylstibinic acid is successively nitrated and hydrolysed with caustic alkali so as to replace the acetylaminocomplex by hydroxyl, the scarlet alkali salt of 3-*nitro*-4-*hydroxystibinic acid* separates. This salt is also produced by converting *p*-chloroaniline into *p*-chlorophenylstibinic acid (by the above diazo reaction). This chloro- compound is nitrated to 3-nitro-4-chlorophenylstibinic acid, which on treatment with alkali exchanges its chlorine atom for a hydroxyl group.



AROMATIC ANTIMONIALS.

Phenylstibine dichloride $C_6H_5{\cdot}Sb{\cdot}Cl_2$, colourless crystals, m.p. 58°; b.p. 290°; very soluble in alcohol, ether, benzene, or light petroleum On warming, the odour, which is at first faint, becomes very pungent and irritating (Hasenbaumer, Ber 1898, 31, 2912)

Phenylstibinic chloride $C_6H_5\,SbCl_4$, is prepared by saturating an ethereal solution of phenylstibine chloride with chlorine, and is obtained as a hygroscopic crystalline mass. It is hydrolysed by water into *phenylstibinic acid*

$C_6H_5{\cdot}SbO(OH)_2$

a white powder decomposing above 200°; insoluble in water; soluble in aqueous alkalis and in glacial acetic acid.

Diphenylstibine chloride $(C_6H_5)_2Sb{\cdot}Cl$, colourless crystals, m.p. 68° (Michaelis and Günther, Ber. 1911, 44, 2316; Morgan and Micklethwait, *l.c.*; Gruthner and Wiernik, Ber. 1915, 48, 1749).

Diphenylstibine trichloride. Colourless needles with one molecule of water, m.p. 180°. Formed as by-product in synthesis I., being extracted with hot dilute hydrochloric acid from the concentrated mother liquors from this reaction. Treated successively with (*a*) alcohol and dilute ammonia, or with (*b*) aqueous sodium hydroxide and acetic acid, the trichloride yields

Diphenylstibinic acid $(C_6H_5)_2SbO{\cdot}OH$, a granular precipitate insoluble in ammonia or sodium carbonate, as produced by the first method, or in a form soluble in these reagents when obtained by the second method.

Triphenylstibine $(C_6H_5)_3Sb$. Colourless, triclinic plates, m.p. 48°; b.p. 231–232°/16–18 mm., above 360°/760 mm. (with partial decomposition); D 1·4998/12° (Ghira, Gazzetta, 1894, 24 (i), 317). Synthesised by method I. (above). The product of this reaction is successively extracted with alcoholic hydrochloric acid and light petroleum, the latter removing the required stibine, which is then precipitated by chlorine in the form of its dichloride, this being reduced by hydrogen sulphide. The product is recrystallised from light petroleum (Michaelis and Reese, Annalen, 1886, 233, 45). An almost quantitative yield can be obtained by employing the Grignard reaction (Morgan and Micklethwait, Chem. Soc. Trans., 1911, 99, 2290).

Triphenylstibine dichloride $(C_6H_5)_3Sb{\cdot}Cl_2$. Formed as a by-product in Method I. (above). Colourless needles, m.p. 143°.

Triphenylstibine sulphide, 'Sulphoform,' $(C_6H_5)_3SbS$. White needles, m.p. 119–120°. Soluble in benzene, chloroform, or glacial acetic acid, less soluble in alcohol, slightly soluble in ether. It has been used successfully in the treatment of eczema and other skin diseases. It is prepared by the carefully regulated action of hydrogen sulphide on the alcoholic ammonia solution of the stibine chloride (Kaufmann, Ber. 1908, 41, 2761)

TERVALENT ANTIMONY DERIVATIVES.

The members of this series of antimonials contain the stibino-group, $-Sb{=}Sb-$, and were discovered in 1911 by the Chemische Fabrik von Heyden, who succeeded in reducing the aromatic stibinic acids.

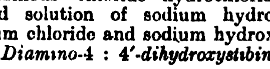
Stibinobenzene $C_6H_5{\cdot}Sb:Sb{\cdot}C_6H_5$. Pale yellow powder, insoluble in water, soluble in glacial acetic acid and chloroform. Phenylstibinic acid in caustic soda solution is cautiously reduced with sodium hydrosulphite, and the resulting crude product extracted with a mixture of alcohol and benzene containing copper-powder. The filtered solution contains the purified product.

3 : 3′-*Diaminostibinobenzene*

$NH_2{\cdot}C_6H_4{\cdot}Sb:Sb{\cdot}C_6H_4{\cdot}NH_2$

Yellow powder, insoluble in water, soluble in glacial acetic acid, soluble with pronounced decomposition in mineral acids. Prepared by treating a dilute alkaline solution of *m*-aminophenylstibinous chloride-hydrochloride with a filtered solution of sodium hydrosulphite magnesium chloride and sodium hydroxide.

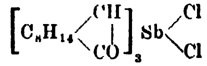
3 : 3′-*Diamino*-4 : 4′-*dihydroxystibinobenzene*



the antimonial analogue of Salvarsan base is prepared by reducing 3-nitro-4-hydroxyphenylstibinic acid with alkaline sodium hydrosulphite. The red colour of the sodium salt of this acid disappears, and the stibinic compound separates as a reddish-brown precipitate, soluble in aqueous alkalis or acids. It is easily acylated, and it condenses with aldehydes. It can be diazotised and yields a colouration with ferric chloride. When oxidised with alkaline hydrogen peroxide it is converted into colourless 3-amino-4-hydroxyphenylstibinic acid (D. R. P. 268451).

MISCELLANEOUS ORGANIC DERIVATIVES OF ANTIMONY.

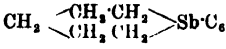
Tricamphorylstibinic chloride



$$\left[C_8H_{14}\begin{matrix}\diagup CH\\ \mid\\ \diagdown CO\end{matrix}\right]_3Sb\begin{matrix}\diagup Cl\\ \diagdown Cl\end{matrix}$$

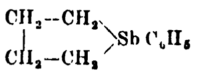
This is the main product of the condensation of the sodium derivative of camphor with antimony trichloride. It is soluble in benzene, from which it is obtained in colourless crystals, melting with decomposition at 244°; it is resolved by water into the unstable *tricamphorylstibinic acid* $(C_{10}H_{15}O)_3Sb(OH)_2$, decomposed by dilute aqueous sodium hydroxide, and by boiling water (Morgan, Micklethwait and Whitby, Chem Soc. Trans. 1910, 97, 35).

Phenylcyclopentamethylenestibine (I) is prepared by the Grignard method from phenylstibine dichloride and the magnesium compound of αε-dibromopentane, and is a colourless, viscous, unpleasant smelling oil, b.p. 169–171°/18–20 mm. (in CO_2); oxidises on exposure to air.



$$CH_2\begin{matrix}\diagup CH_2\cdot CH_2\diagdown\\ \diagdown CH_2\cdot CH_2\diagup\end{matrix}Sb\cdot C_6H_5$$

I.



II.

When αδ-dibromobutane is employed in this condensation *phenylcyclotetramethylenestibine* (II.) is obtained as a colourless oil of unpleasant odour, b.p. 156–158°/20-22 mm., yielding crystalline dichloride and dibromide (Gruttner, Wiernik and Krause, Ber. 1915, 48, 1473; 1916, 49, 437).

Bibliography.—Organic Compounds of Arsenic and Antimony (Morgan, London, 1918).

G. T. M.

ANTIMONIN. Trade name for antimony calcium lactate, used as a tannin-fixing mordant.

ANTIMONITE. Native antimony sulphide (*v.* ANTIMONY).

ANTIMONY. (*Antimoine*, Fr.; *Antimon*, Ger.) *Stibium.* Sym. Sb. At.wt. 120·2.

Occurrence.—Antimony occurs native in small quantities, occasionally in rhombohedral crystals, at Andreasberg in the Hartz, Przibram in Bohemia, Sala in Sweden, Allemont in France, in the United States, New South Wales, and Quebec. It occurs in large masses in Sarawak, Borneo.

Combined with *oxygen* as the sesquioxide Sb_2O_3, it occurs in *antimony bloom, white antimony*, or *valentinite*, and in *senarmontite*, being found in workable quantities in the Algerian province of Constantine. In *antimony ochre* or *cervantite*, and in *stibiconite* and *volgerite*, it occurs as antimonite of antimony Sb_2O_4.

Combined with *sulphur*, it occurs as *stibnite, antimonite*, or *grey antimony ore* Sb_2S_3. In union with *sulphur* and *oxygen* together, it forms *red antimony, antimony blende* or *kermesite* $Sb_2O_32Sb_2S_3$.

With *arsenic*, antimony is found in *allemontite* or *arsenical antimony*. With *silver*,

With sulphur and metals, antimony forms a number of *sulphantimonites*, among which may be mentioned *zinkenite, jamesonite, boulangerite* and *feather ore*, containing antimony, sulphur and lead; *miargyrite, pyrargyrite*, and *stephanite*, containing silver; *berthierite*, containing iron, and *antimonial copper glance*. Antimony is found in certain ferruginous waters.

The antimony minerals of commercial importance as ores are *stibnite*, and the decomposition products which are usually associated with it and sometimes entirely replace it, viz. *kermesite, valentinite, senarmontite*, and *cervantite*.

Antimony ores occur in workable quantities in Mexico, California, North and South America, Canada, Australia, Japan, Borneo, Cape of Good Hope, New Zealand, Asia Minor, Austria Hungary, France, Russia, Siberia, Serbia, Algiers, Italy, Spain, Portugal, Corsica, and Sardinia. Small deposits of antimony sulphide have been discovered in Cornwall, Cumberland and Scotland.

Antimony ores occur in the south of Hupeh and part of Sze-chuen province and in the provinces of Hu-nan Kwei-chow, Kwang-si, and Yun-nan. Roughly speaking, this vast antimony belt comprises the entire western half of China south of the Yang-tse-Kiang. There are smelting and refining works at Woo-chow which reduce the ore mined in the province of Kwang-si, exports from which are shipped to Canton and Hong-Kong. There are also important works at Chang-sha, the capital of Hu-nan province, exports from which are shipped *viâ* Hankow and Shanghai (Schoeller J. Soc. Chem. Ind. 1913, 32, 260).

For a list of antimony-producing countries *see* J. Soc. Chem. Ind. 1915, 34, 1148.

The veins in which stibnite is found are usually 4–6 inches in width, but in some rich mines, as in Nevada, they are several feet across. The gangue materials are quartz, with some brown-spar and heavy spar, and from these the sulphide can only be separated by hand picking or liquation. It is occasionally found in pockets, when it is usually very pure.

By far the most general ore of antimony is the sulphide, but in some cases, as in Algeria, the oxide is found in workable quantities, and in other cases both oxide and sulphide occur together.

Extraction.—Metallic antimony and its compounds are nearly always extracted from the ores by dry methods. According to their suitability for the several methods of treatment the ores fall into two broad classes:

(*a*) Sulphide ores containing over 40 p.c. stibnite.

(*b*) Sulphide ores containing less than 40 p.c. of the sulphide, and oxide ores of any grade. In this class also may be included liquation residues and flue deposits, &c.

Preliminary treatment of Ores.—Ores of class (*a*) are used for the production of the metal by the English process. If the content of sulphide is over 90 p.c., the ore requires no preliminary treatment, but less pure ore is subjected to a process of *liquation*, in which the sulphide is melted and allowed to run away from the gangue.

formerly used where fuel is plentiful, as at Malbosc, in the Department of Ardèche, Wolfsberg in the Hartz, and in Hungary. The ore was placed in small lumps in a number of conical pots of 45 kilos capacity, each perforated below and standing on a perforated plate over a sunken receiver. The pots were surrounded by fuel which continued to burn for 10 hours, the melted sulphide, known as crude antimony, collecting in the receivers.

At La Lincouln, Wolfsberg, and Haute Loire, the pots were contained in a reverberatory furnace. At Schmöllnitz, in Hungary, the melted sulphide ran through channels into receivers outside the furnace.

At Malbosc, the pots are replaced by cylindrical tubes, perforated below and standing on similarly perforated plates above the receivers. Each cylinder has a capacity of 500 lbs. of ore, four being heated in one furnace. Each has a hole at the side, through which the residues are removed, these holes being closed during the heating. The receivers are of clay, or of iron coated with clay.

At Chang-Sha, and also in other parts of the province, crude antimony is obtained from high-grade (58 p.c.) ores by liquation. The process is carried out in furnaces each of which holds two clay crucibles, the charge for each crucible being 50 lbs. of ore. The crucibles are inclined and perforated at the bottom; they are fired for two hours, the liquated sulphide collecting in a cavity at the back of the furnace, whence it is ladled into iron moulds and allowed to solidify. The pasty liquation residue is dumped into loose iron frames formed of two L-shaped pieces in which it cakes together on cooling (Schoeller, *l.c.*).

The method of liquation in reverberatory furnaces is used in some places where ore can be mined cheaply but fuel is dear. The consumption of fuel per unit of sulphide liquated is least with this type of furnace, but there is a considerable loss of antimony by volatilisation. This loss, however, can be prevented by the use of suitable condensing apparatus such as Herrenschmidt's (*v.i.*).

In any process of liquation the temperature must be carefully regulated, as too low a temperature results in a low yield of sulphide, the residues containing too much antimony, while too high a temperature increases the loss by volatilisation.

The liquated stibnite contains much less sulphur than is required by the formula Sb_2S_3, and Schoeller has shown that this is due to the presence of oxygen.

Ores of class (*b*) are either roasted to the non-volatile tetroxide, or to the volatile trioxide, or are subjected to one of the direct reduction processes.

The oxidation of the sulphide to tetroxide takes place at temperatures between 350° and 400° in presence of excess of air. If the ore is impure, antimonates of the metallic impurities are formed at the same time. During the roasting there is a great tendency for the ore to frit, and this necessitates the constant rabbling of the charge. The presence of gangue renders the ore less liable to fuse, so that the process is most easily carried out with poor ores, *e.g.* ore-dust, for the treatment of which it is largely used. The furnaces employed are of two classes:

(*a*) Hand rabbled reverberatory furnaces, having an egg-shaped flat bed, with a fireplace on either side and a working door at the front. With these the process is intermittent.

(*b*) Long bedded furnaces, in which the roasting is carried on continuously. These furnaces are 40–45 feet long, by 8 feet wide, by 2 feet high, and have 10 working doors on each side. The ore is charged in at one end, and is then gradually worked along the bed during about 40 hours, and finally discharged at the other end. Fresh ore is continually charged into the furnace at the rate of 6 cwts. every 8 hours.

The oxidation of the sulphide to volatile trioxide takes place at about 400° with a carefully regulated amount of air. This process, provided suitable condensation apparatus is installed, presents marked advantages, and is finding an increasing application, especially in dealing with poor ores. It may be noted that arsenic is completely separated as the more volatile trioxide, that any gold or silver present is left in the residue and can afterwards be extracted, that the loss of antimony and the consumption of fuel are low. Many different forms of plant have been used for this process, but in most the roasting takes place in a furnace of cupola type, the most important processes being the Chatillon and Herrenschmidt. The forms of condensing apparatus are of two classes:

(*a*) In which the vapours are passed through a series of flues and chambers and finally through water-tanks in which the last traces of oxide are deposited.

(*b*) In which the furnace gases are cooled below 100° in flues and then filtered through canvas or other coarse fabric.

In the Herrenschmidt process the roasting furnace is built of brick, and is provided with a hopper through which the ore, mixed with 4–5 p.c. of gas-coke or 6–7 p.c. charcoal, is introduced. The gases pass from the furnace into a chamber, and then through a series of cast-iron tubes placed nearly vertical and air-cooled, in which the main portion of the trioxide is deposited. The last traces are removed by forcing the gases up a tower filled with coke over which water flows. The draught is maintained by two centrifugal fans, working tandem. It is stated that 6 tons of ore, containing 10–15 p.c. antimony, can be treated in 24 hours, with a yield of over 90 p.c.

Smelting of the metal.—Antimony is prepared from 'crude antimony' or high-grade stibnite ores by the 'English' or 'precipitation' method. The ore, of which the composition has been determined by analysis, is ground under edge-runners to the size of a hazel-nut, or smaller, and is subjected to three operations:

Singling. This process is carried out in crucibles of which about forty are arranged in a double row on the hearth of a long reverberatory furnace having a grate at each end, and a flue, leading to condensing chambers, in the middle. The crucibles are about 20 inches high and 11 inches across, and are made of a mixture of 6 parts fire-clay and 1 part plumbago. The charge for each pot is 42 lbs. ore, 16 lbs. iron, 4 lbs. salt, and 1 lb. slag from 'doubling' (*v.i.*). These materials are introduced into the red-hot crucible, and kept in a state of fusion for 2–3 hours, at the end of which time the contents are poured into moulds, and the antimony is removed from beneath the slag. The product, known as *singles*, usually contains about 91 p.c. antimony.

Doubling is carried out in crucibles arranged in a furnace as previously described. The charge for each pot is 84 lbs. broken singles, 7–8 lbs. liquated sulphide, and 4 lbs. salt, and the fusion, which takes about 1½ hours, is closely watched, the workman judging from the nature of the slag when the operation is complete. The slag is then removed with an iron ladle, and the metal poured into moulds. This product is called *bowl metal* or *star bowls*, and sometimes contains over 99 p.c. antimony.

Starring, or *melting for star metal* (*v.i.* under *Refining*).

In the English process the loss due to slagging and volatilisation is small, being only 2–5 p.c.

It is possible also to reduce the sulphide on the hearth of a reverberatory furnace. The partially roasted ore, which contains the sulphide and oxides of antimony, is mixed and fused with 8–13 p.c. of coal and 9–11 p.c. of soda, frequently with the addition of iron, in which case the slag produced is much less fusible and does not entirely cover the bath of metal; the antimony produced also contains much iron (Dingl. poly. J. 162, 449). Where carbonate of soda is used for the fusion the mass froths considerably and attacks the furnace hearth.

The metal is prepared from either of the oxides by one of the numerous reduction processes now in use.

(*a*) Reduction in reverberatory furnaces is carried out at Bouc, Septêmes, New Brunswick, &c. The furnace-bed is egg-shaped, deep in proportion to its width, and is provided with a tap-hole at the lowest point. The furnace gases are passed through a long series of condensing chambers. First 90–110 lbs. flux (chiefly salt, with some soda and sodium sulphate) and 220–230 lbs. of slag from a previous operation are melted on the hearth, and then 400–500 lbs. of roasted ore and 67–75 lbs. of charcoal are added, and the whole kept in a state of fusion till reduction is complete. At New Brunswick the reduction and refining are carried out consecutively in the same operation.

(*b*) Some French smelters reduce an oxidised ore containing 30–40 p.c. of antimony in a 3-tuyered shaft furnace at the rate of 2–2½ tons per 24 hours, with the consumption of about half that weight of coke. The regulus contains 92–95 p.c. of antimony, and is subsequently refined.

At Bánya, Hungary, antimony ores are mixed with silicious material and smelted in a blast-furnace for impure regulus, which is then refined in a reverberatory furnace. The blast-furnace used is a round stack 6 m. high and 1·4 m. diameter at the throat. The hearth, which is 1 m. across, is fitted with five water-jacketed tuyeres, and has two outlets for slag and metal respectively; a third opening is used for blowing out. A blast of 15 c.m. per minute is used, and the gases are collected by a tube at the throat and passed through a condensing apparatus. Such a furnace will run for 3 weeks continuously, smelting about 20 tons of material daily (Berg. u. Hütt. Zeit. 1886, p. 102).

(*c*) Reduction in crucibles is only used when rich ore or the trioxide is available. The reducing agent for the trioxide is carbon (charcoal or anthracite), and sodium sulphate and carbonate are added to form a slag.

Considerable quantities of antimony ore are now treated directly for the production of the metal. One such process which has been successfully used for some time depends on the reduction of the sulphide in a bath of molten ferrous sulphide containing iron (*v.* T. C. Sanderson, U.S. Pat. 714040, 1902; Cookson, Fr. Pat. 324864 1902; and Herrenschmidt, Fr. Pat. 296200, 1900).

Another method consists in the reduction of the sulphide with carbon in water-jacketed blast-furnaces. This has been used by Hering for the treatment of liquidation residues.

W. R. Schoeller (Bull. Inst. Min. and Met. Feb. 1918) describes the blast-furnace smelting of antimony ores direct in water-jacketed blast furnaces, the charge consisting of ore, basic slag, chalk and coke. In this method, no iron is added to the charge and no reduction of iron takes place in the furnace. The antimony is obtained as a high grade metal, practically free from iron. The best conditions for working the furnace are found to be about 10 p.c. coke, low blast pressure, low metal content of charge (about 10 p.c.), high smelting column (over 15 feet), and provision of a heated forehearth for the separation of metal and slag.

Methods of treating antimony ores have also been proposed by which the antimony is converted into the volatile chloride, as in Lyte's process of roasting the ore with salt. The ore may also be subjected to the action of hydrochloric acid gas in a reverberatory or muffle furnace, the volatilised chloride being condensed in a solution of hydrochloric acid (Dingl. poly. J. 250, 79–88, and 123–133).

Among processes allied to the smelting of antimony there need only be mentioned that of Herrenschmidt for the extraction of gold from antimony (Fr. Pat. 350013, 1904). This depends on the fact that when a small quantity of antimony is melted with or reduced from auriferous stibnite, all the gold present in the sulphide passes into the metal.

Many proposals have been made for the extraction of antimony by wet or electrolytic methods, but they have not been a success commercially. Reference may be made to Hering (Dingl. poly. J. 230, 253), and Borchers (Electrolytische Gewinnung des Ant. Chem. Zeit. xi. 1883, 1023).

Refining of Antimony.

Unrefined antimony contains sulphur, iron, arsenic, and sometimes copper, gold, and lead. The following analyses show the composition of typical samples, I. and II. being metal made with scrap iron; III. and IV. metal from roasted ore smelted in a blast furnace; V. Chinese:—

	I.	II.	III.	IV.	V.
Antimony .	94·5	84·0	97·2	95·0	98·20
Iron . .	3·0	10·0	2·5	4·0	0·146
Sulphur .	2·0	5·0	0·2	0·75	0·37
Arsenic .	0·25	1·0	0·1	0·25	0·148
Gold .	traces	—	—	—	—

All these impurities, except lead, can be removed by slagging with oxidising, sulphurising, or chlorinating agents. The usual fluxes are: Glauber salt and charcoal, which remove copper and iron as sulphides, and arsenic as sodium arsenate; and antimony glass (antimony oxysulphide) which eliminates sulphur. Chlorides, such as salt or carnallite, must be used with caution, or great loss by volatilisation may result.

Refining in crucibles finds its chief application in the English process. The 'star bowls' (*v.s.*) are cleaned from slag by chipping with sharp hammers, and the metal is then broken small and melted with 2–3 p.c. of antimony flux, prepared by melting together American potashes and powdered stibnite in varying proportions (approximately 3 parts potashes and 2 parts stibnite) until, by experiment, the correct composition is found. The refining is carried out in the pots nearest the grates, and takes 30 minutes to 1 hour, the charge for each crucible being 84 lbs. The finished product is run into 8-lb. ingots, which are carefully covered with slag and allowed to cool without disturbance. The coal consumption is large, but is compensated by a much smaller loss by volatilisation than occurs in other processes.

Refining in reverberatory furnaces is used at Milleschau, Bánya, Siena, and Oakland. It is imperative that the bed of the furnace should be tight and able to withstand the action of the alkali flux, and this is best attained by making it of one solid piece of soft, weathered granite. A fairly good substitute for the granite is a mixture of burnt and raw clay well rammed into an iron box. An example of such a process is that recommended by Helmhacker and used at Milleschau (Berg. u. Hütt. Zeit. 1883, 191; and Dingl. poly. J. 250, 123).

A 'glass of antimony' is prepared by fusing a mixture of the crystalline antimony oxide which collects on the hotter portions of the flues with sulphide of antimony, until it forms a glassy dark grey or brown mass; this is mixed with the carbonate for the purification of the metal, and is occasionally used alone where the metal is but slightly impure

The bed of the furnace is heated to a cherry red and 600 to 700 kilos. of crude antimony placed on it; a quantity of oxide and some arsenic escape, and in from 30 to 60 minutes the metal has run down. From 3 to 7 p.c. (according to the purity of the metal) of carbonate of soda, sometimes mixed with coal or coke, is then added The metal is thus covered and fumes less, small jets of flame appearing occasionally on its surface; the temperature is raised, the metal remaining under the slag for from 1 to 3 hours (determined by the workman), the slag then becomes thick, and is removed by drawing it through the door with a long-handled flat transverse iron.

Three p.c. of antimony sulphide and 1½ p.c. of oxide are then thrown on the surface of the metal, and when melted 4½ p.c. carbonate of potash, or of a mixture of carbonate of potash and soda, are added. By this means the iron and last traces of sulphur are removed; in less than 15 minutes the refining is complete, and the critical operation of ladling is performed. A cast-iron hemispherical ladle, holding 15–20 kilos., is riveted to a chain hanging from the roof exactly in front of the working door, before which the cast-iron moulds for receiving the metal are arranged on a stone table. The workman dips his ladle obliquely, removing some slag with the metal; part of this is first poured into the mould to prevent the metal from actually touching the mould, and the metal is well covered with the slag and left at rest. Unless this be done the 'starring' will be imperfect, and, as this is considered a test of purity, its value will be lowered in the market. The slag may generally be used again. The oxide condensing in the flues is removed as seldom as possible, as this operation, as well as the furnace work, is very injurious to the workers.

Star antimony usually contains small amounts of iron, lead, sulphur, and arsenic, but can be further purified by Liebig's method, which consists in fusing the metal successively with 12 p.c. sodium carbonate and 6 p.c. antimony sulphide, and again with sodium carbonate to which a little nitre has been added.

The following are typical analyses of commercial antimony (*v.* Min. and Sci. Press, July 10, 1915).

	Cookson's	Hallett's.	Japanese.	Chinese.
Lead .	0·041	0·669	0·424	0·018
Tin .	0·035	0·175	0·012	0·035
Arsenic .	trace	trace	0·095	0·017
Copper .	0·040	0·038	0·043	0·008
Iron .	0·010	0·014	0·007	0·007

When 'pure,' and cast under correct conditions, a beautiful fern leaf or 'star' appears upon the surface of antimony, and according to the length and form of this 'star' on the ingot its quality is decided. Although the 'star' is accepted as a criterion for the purity of the metal, it is really only a rough guide. It is no guarantee that the metal is more than 99 p.c. pure, as it may be produced with inferior metal, while the very best metal may show an imperfect star or none at all if not properly cast. It is this peculiar characteristic of pure antimony to crystallise on the ingot in the fern-leaf or star form when cooling, which originates the trade term of 'star antimony' for good quality of antimony.

For pharmaceutical purposes it is important to prepare antimony quite free from arsenic. This may be accomplished by Wöhler's method. A mixture of 4 parts powdered commercial antimony, 5 parts sodium nitrate, and 2 parts sodium carbonate (to prevent the formation of insoluble antimony arsenate) is thrown into a red-hot crucible. Combustion takes place quietly, the mass is pressed together and more strongly heated for half an hour, so as to become pasty without fusion, being pressed down as it rises from evolution of gas. While still hot and soft, it is removed, reduced to powder, and boiled with frequent stirring in water, the finer powder is poured off with the water, and the residue again treated, the washings being mixed with that first obtained. The water, which contains the whole of the arsenic but no antimony (Meyer), is removed from the insoluble portion by subsidence, decantation, and filtration. The residue of sodium antimonate should be white but the presence of lead imparts a yellow colour It is dried and fused with half its weight of cream of tartar at a moderate heat, cooled, broken into small lumps, and the potassium and sodium removed by digestion in water. The powdered metal is then fused into a button.

This method may be used quantitatively for the separation of antimony from arsenic. If the sodium nitrate be replaced by potassium nitrate, a portion of the antimony will enter into solution with the arsenic as potassium antimonate (*v.* C. Meyer, Annalen, 46, 236; Chem. Zentr. 1348, 828). Arsenic may also be completely removed by fusing the antimony in succession with 1st, potassium carbonate; 2nd, potassium nitrate; 3rd antimonic oxide; 4th, potassium carbonate (Th. Martins, Kastn. Arch. 24, 253), or by fusing three times with fresh portions of sodium or potassium nitrate.

Duflos (Kastn. Arch. 19, 56) recommends a process in which the arsenic is driven off as fluoride by means of sulphuric acid and fluorspar. (*See* further Schw. 42, 501; also Buchner and Herberger, Repert. 38, 381, 256.)

Pure antimony may be obtained by heating tartar emetic to low redness and digesting the resultant mass in water to remove the potassium. The powder thus obtained may be then dried and fused into a button.

Groschuff (Zeitsch. anorg. Chem. 1918, 103, 164) describes the following method of preparing chemically pure antimony. Antimony trichloride or pentachloride is purified by distillation and converted into chloroantimonic acid. The chloride is dissolved in concentrated hydrochloric acid, and chlorine is passed in until the solution becomes greenish-yellow, and then hydrogen chloride is introduced. After purification by recrystallisation, the chloroantimonic acid is hydrolysed to antimonic acid, which is reduced to metal by fusion with potassium cyanide.

Tests for Impurities in Antimony.

Sulphur. The powdered metal evolves sulphuretted hydrogen gas (which blackens lead paper) on heating with strong hydrochloric acid.

Arsenic. If deflagrated with ¼ its weight of sodium nitrate, boiled with water and filtered, the arsenic enters into solution, leaving the antimony behind; the solution is saturated with sulphuretted hydrogen (if an orange precipitate, consisting of antimony sulphide, falls, this must be filtered quickly; it is due to the presence of a trace of antimony in the solution). The arsenic is deposited as the lemon-yellow sulphide on standing.

Lead and copper. The metal is powdered and treated with dilute nitric acid, evaporated nearly to dryness, taken up with water and filtered; the addition of sulphuric acid precipitates white lead sulphate, and the addition to the filtrate of potassium ferrocyanide gives a brown precipitate in presence of copper.

If sulphur as well as lead be present in the antimony, the lead is converted at once into sulphate by the action of nitric acid, the residue on evaporation is digested with yellow ammonium sulphide, which dissolves the antimonic oxide and leaves black lead sulphide.

Iron. The powdered metal is ignited with three parts nitre and washed with boiling water, the residue is boiled with hot dilute hydrochloric acid; on the addition of potassium ferrocyanide a blue precipitate is produced.

Detection of antimony. When fused on charcoal with potassium cyanide or sodium carbonate or a mixture of the two, antimonial compounds produce a brittle white bead of metallic antimony with white fumes and a white incrustation on the charcoal; the bead leaves a white residue on treatment with nitric acid, which is soluble in cream of tartar or tartaric acid. Sulphide of antimony melts readily in the candle flame.

A delicate confirmatory test, given by Crookes, is to add to the white incrustation on the charcoal one drop of ammonium sulphide, when the formation of the orange sulphide is conclusive evidence of the presence of antimony.

Estimation of antimony.—Wet assay.—(*a*) *Gravimetric.* In the case of ores and products, a weighed quantity is fused with sodium hydrate and a little potassium nitrate, the fused mass is extracted with water and a little hydrochloric acid if necessary. The solution obtained is filtered, and if much residue remains, it is re-fused. A few grammes of tartaric acid and excess of oxalic acid are added, and hydrogen sulphide is passed through the solution first cold and then after heating. The sulphide precipitate is filtered off and digested with sodium sulphide and filtered. To the solution, hydrochloric acid and potassium chlorate are added, and it is boiled until free from chlorine. The acidity of the solution is adjusted to 50 p.c., hydrochloric acid and hydrogen sulphide passed to precipitate arsenic, which, if present, is filtered off. The solution is diluted to three times its volume, and is ready for the precipitation of the antimony. In the case of alloys containing antimony, these are dissolved in hydrochloric acid with the aid of potassium chlorate to the solution, excess of tartaric acid is added, and it is poured into a solution containing soda in excess. The solution is digested, filtered, and the precipitate washed with sodium sulphide solution. The filtrate is acidified with hydrochloric acid, potassium chlorate is added, it is then boiled until free from chlorine, and excess of oxalic acid is added. In either case hydrogen sulphide is now passed into the cold solution for 20 minutes. Then, without stopping the current of gas, the solution is heated to boiling, and the gas allowed to pass for another 15 minutes. The resulting precipitate of sulphide may then be subjected to one of two methods of treatment. It may be collected on a Gooch crucible, washed with hot dilute acetic acid, saturated with hydrogen sulphide, and heated to constant weight at 230° in a current of carbon dioxide. Or the precipitate may be collected on a filter, washed successively with hot water, alcohol, equal parts alcohol and carbon disulphide, alcohol, and, finally, ether, and then dried. The greater part of the precipitate is transferred to a watch-glass, and that still adhering to the paper is dissolved in a little hot ammonium sulphide, and the solution allowed to run into a weighed porcelain crucible. This is then evaporated to dryness, the main portion of the precipitate added, and the whole treated with fuming nitric acid and warmed, the crucible being covered with a watch-glass. When the violent action has subsided, the contents of the crucible are evaporated to dryness, again treated with nitric acid, and finally evaporated to dryness and heated to redness till the weight is constant. The antimony is then weighed as tetroxide.

(*b*) *Volumetric*. The most important volumetric method is that of Möhr, in which antimony trioxide or any antimonious compound is dissolved in a solution of tartaric acid, neutralised with sodium carbonate, treated with a cold saturated solution of sodium bicarbonate in the proportion of 10 c.c. to each 0·1 gram Sb_2O_3, and quickly titrated with *N*/10-iodine solution, using starch as indicator.

(*c*) *Electrolytic*. Classen and others have shown that if antimony sulphide (*v.s.*) is dissolved in the minimum amount of concentrated solution of sodium sulphide, and treated with excess of sodium sulphite, or, better, potassium cyanide solution (to destroy polysulphides), the liquid can be successfully electrolysed in the cold with a current of 0·25–0·5 amp., using a platinum dish as cathode. The process takes about 12 hours, and gives a good coherent deposit of metal which can be washed with water, alcohol, and ether, and finally dried and weighed.

Properties of Antimony.

Antimony is a lustrous, bluish-white metal, which has a coarsely laminated or granular structure, according as it has been slowly or quickly cooled. By partial solidification it can be obtained in obtuse rhombohedra, approximating to cubes.

The sp.gr. of the metal is 6·72–6·86. It melts at 630·5° C. (Heycock and Neville, Chem. Soc. Trans. 1895, 186), and boils at about 1500° C. in a current of hydrogen. Antimony has a hardness of 3–3·5, and is so brittle that it can readily be powdered. It is a bad conductor of heat and electricity.

The most important physical property of antimony is that of expanding on solidification, a property possessed also by its alloys. At the ordinary temperature it is not acted on by the air, but oxidises quickly on melting, and burns at a red heat, producing white fumes of the trioxide. It is oxidised by nitric acid of various strengths, dilute acid producing principally the trioxide, and the concentrated acid producing the pentoxide (H. Rose, Analyt. Chem. 1, 258). Dilute sulphuric and hydrochloric acids are without action on it, but the strong acids produce the sulphate and chloride respectively. When fused with borax or other vitrifying material, it imparts to them a yellow colour.

Antimony combines directly with the halogens with evolution of light and heat, and also, at a higher temperature, with the elements of the sulphur group, and with phosphorus and arsenic. The element occurs in three modifications: (1) the crystalline or ordinary form described above; (2) an amorphous yellow modification, soluble in carbon disulphide, which is produced by the action of oxygen on liquid stibine at −90°; and (3) the amorphous explosive antimony, which is best prepared by the action of a weak constant electric current on a concentrated acid solution of antimony trichloride, the strength of current bearing a constant relation to the surface of deposition, not less than ½ grain being deposited per sq. inch per hour. Thus produced, it is bright and steel like in appearance, with an amorphous fracture and sp.gr. 5·78. When heated to 200°, or struck or scratched, it rapidly changes into the crystalline form, increasing in density, with the production of great heat. Antimony trichloride is always contained in the metal to the extent of 4·8–7·9 p.c., and is given off when the form changes. It is probable that this substance is a solid solution of an antimony halogen compound in an allotropic form of antimony, and that the explosion consists in the rapid transformation of the latter into the stable form. The change is accompanied by an evolution of heat amounting to 20 cals. per gram. Cohen and others (Zeit. physikal. Chem. 1904, 47, 1; 1905, 50, 291; 52, 129) have shown that this change goes on slowly when explosive antimony is preserved.

Antimony is precipitated as a fine powder by the action of zinc on an acid solution of an antimony salt. In this form it is sold as 'iron black' for producing an appearance of polished steel on papier maché, plaster of Paris, and zinc ornaments.

Brass can be covered with a fine lustrous coating of antimony by dipping in a hot mixture of 1 part tartar emetic, 1 part tartaric acid, 3 or 4 parts powdered antimony, 3 or 4 parts hydrochloric acid, and 3 parts water.

It may be deposited electrolytically on brass or copper by using a bath of the double chloride of antimony and ammonia acidulated with hydrochloric acid.

Alloys of Antimony.

Antimony alloys with most of the heavy metals and with the alkali metals. It dissolves in a solution of sodium in liquid ammonia. It generally increases the fusibility, brittleness, and hardness of the metals with which it is alloyed, and imparts the valuable property of expanding on solidification, thus producing very fine impressions. The sharpest impressions are produced when any of these alloys are cast at a low temperature (J. Soc. Chem. Ind. 1, 982). The castings are usually made in brass moulds coated with lampblack and turpentine.

With *lead*, antimony alloys readily in all proportions. An alloy of equal parts of lead and antimony is very brittle, and rings when struck. Nasmyth has recommended the addition of 5 p.c. antimony to lead for use instead of bronze in taking casts of works of art (Athenæum, No. 1176, 511).

Type metal is essentially an alloy of lead and antimony, frequently with addition of tin and containing less frequently copper. A few examples of common type-metals are.

	Lead	Antimony	Tin	Copper
Type metal .	55	30	15	—
„ . .	70	18	10	2
„ .	77·5	16	6·5	—
„ .	82	15	3	—
Stereotype plate .	85·7	14·3	—	—
„ „ .	82·5	13	4·5	—
Linotype metal .	84·5	13·5	2	—
„ „ .	83	12	5	—

The alloys, containing varying proportions of antimony, are also used, under the name of hard lead, in lead pipes, for making pumps and taps for raising acid in alkali works, in the manufacture of shrapnel and shot, and for the emery wheels and tools of the lapidary.

Tin forms numerous useful alloys with antimony, especially with the addition of other metals. *Common Britannia metal* contains tin 94, copper 1, antimony 5. Britannia metal for castings: tin 90·6, copper 0·2, antimony 9·2. The best Britannia metal contains tin 90, antimony 10, lead and bismuth being carefully excluded. Copper also is never added except for the production of colour. Increasing the proportion of antimony raises the m.p., increases the hardness, and decreases the malleability of the alloy. Good alloys take a brilliant polish, and show a fine-grained, jagged fracture. The presence of arsenic in the antimony diminishes the ductility of the product.

Metal argentum contains tin 85·5, antimony 14·5.

Ashbury metal: tin 77·8, zinc 2·8, antimony 19·4. Ships' nails, tin 50, lead 33, antimony 17.

Minofer is tin 68·5, antimony 18·2, copper 3·3, and zinc 10.

Bearing or *anti-friction metal* usually contains antimony, tin, lead and copper, but the composition is very variable. As the name indicates, it is used for machinery bearings, being especially suitable for light loads at high speeds. As examples of these alloys the following may be given:—

	Antimony	Tin	Copper	Lead
Babbit's metal . .	8·3	83·3	8·3	—
Railway bearings .	15	8	2	75
,, ,, .	13·5	11·5	3	72
,, ,, .	10	51	2	37
U.S. Rly. Babbit metal	7·4	88·9	3·7	—
German Rly. Babbit metal . . .	11·1	88·3	5·6	—

Copper. The presence of 0·15 p.c. of antimony renders copper both cold and hot short. With varying proportions of the two metals, shades from pure copper-red to rose-red, crimson, and violet may be obtained, the last when equal parts of each are present. Two definite compounds of copper and antimony appear to exist, viz. $SbCu_2$, a violet alloy known as 'Regulus of Venus,' and $SbCu_4$ (Kamensky, Phil. Mag. [5] 17, 270; *v.* also Ball, Chem. Soc. Trans. 1888, 167).

Antimony is sometimes added to brass to heighten its colour. These alloys are harder and finer in texture than copper or brass, and take a better polish, and are sometimes used for concave mirrors.

Zinc. Antimony forms alloys with zinc, which decompose water rapidly at the boiling temperature, and this action is promoted by the presence of traces of platinic chloride. Cooke has suggested the suitability of this reaction for the preparation of pure hydrogen.

Melted gold absorbs the vapour of antimony, but gives it up almost entirely on further heating. Gold loses its malleability when $\frac{1}{2000}$ of antimony is present. An alloy of 9 gold and 1 antimony is white and very brittle, with an amorphous porcelain-like fracture. Silver antimonide occurs as the mineral *discrasite*. C. O. B.

Compounds of Antimony.

The principal compounds of antimony are formed by combination with oxygen, sulphur, and chlorine; some compounds contain two of these negative elements, of which the oxychloride or *powder of Algaroth*, and the oxysulphide or *glass of antimony* are examples.

The most important of these are the trichloride, trisulphide, and trioxide.

Antimony trisulphide Sb_2S_3.

Crude antimony, antimony ore, sesquisulphide of antimony; Schwefelspiessglänz; Grau-Spiessglanzerz; Stibium sulphuratum nigrum; lupus metallorum.

This substance, as it occurs naturally, or after liquation, is usually too impure to be employed for other purposes than the preparation of the metal.

The ordinary sulphide may be prepared by the following methods:—

(1) Thirteen parts pure antimony are mixed with 5 parts flowers of sulphur, and projected in portions into a red-hot crucible; when completely fused, it is poured out and any free metal detached.

(2) Sulphuretted hydrogen precipitates it as an orange precipitate from a solution of an antimony salt.

(3) Digest for two hours in a closed vessel 1 part crude antimony sulphide, 1 part pearl ash, 1½ parts lime, and 15 parts water, and add sulphuric acid; the alkaline sulpho- salt first formed is decomposed by the acid with the precipitation of the pure sulphide. Antimony sulphide is soluble in alkaline sulphides and in acid potassium sulphate. When finely powdered and rubbed to a paste at 20° or 30° with strong sodium sulphide solution, a coppery metallic mass is produced, and the liquor, on addition of more sodium sulphide, yields Schlippe's salt.

The sulphide is used to some extent in refining gold from silver and copper, and in the preparation of safety matches and percussion pellets for cartridges, in pyrotechny and in veterinary surgery.

Kermes mineral. *Brown-red antimony sulphide. Pulvis Carthusianorum. Sulph. stibiatum rubrum.*

Kermes mineral usually consists of a mixture of the trisulphide and trioxide containing alkali. Berzelius and Rose state that some samples examined by them consisted of a true double sulphide of potash and antimony.

Preparation.—Fuchs asserts that if antimony sulphide is heated and *suddenly* cooled in water it yields an orange-red, less dense powder of kermes. A. Ditte (Compt. rend. 102, 212) does not confirm this statement.

(1) Four parts pure potassium carbonate and 11 parts pure antimony sulphide are heated to fusion in a covered crucible, cooled, boiled with water, and filtered. The solution on exposure to the air deposits kermes, the residue from the first boiling is heated with the mother liquor from some previously deposited kermes, and yields a further quantity; this operation is repeated until an insoluble residue of trisulphide and trioxide is left. Each successive deposit of the kermes contains a larger amount of the oxide.

(2) Fuse together 2 parts antimony, 1 sulphur, and 3 sodium carbonate; or, 1 antimony sulphide and 3 or 4 tartaric acid, until fumes cease to be evolved; and treat the product as in (1).

(3) The slags from the reduction of antimony ore with cream of tartar slowly precipitate

kermes when treated with water; this is sold to veterinary surgeons as ‘kermes by the dry way.’ When antimony sulphide is boiled with potash and precipitated with an acid, the kermes produced contains no oxide (Liebig). The kermes produced by the action of *dilute* alkaline carbonate on antimony sulphide also contains no oxide (Rose). The oxide may be removed from ordinary kermes by digestion with tartaric acid. A solution containing so much alkali as to give no precipitate on cooling gives, when treated with carbonic acid gas, a highly sulphurated kermes containing antimony pentasulphide.

Kermes is a brown-red, loosely coherent powder, with a brown streak, containing water, which is given off below 100°. It is lighter than the ordinary sulphide. The kermes containing antimony oxide, when fused and solidified, is destitute of crystalline structure, while that free from oxide produces a highly crystalline solid.

Antimony pentasulphide Sb_2S_5. *Golden sulphide of antimony; sulphur antimonii auratum.*

Prepared by boiling the trisulphide with potash and ground sulphur, filtering and precipitating with acid. Redwood recommends 4 parts black antimony sulphide, 8 lime, and 80 water, digested, filtered, and precipitated with hydrochloric acid; or, 2 sulphide, 4 potassium carbonate, and 1 sulphur, to be fused, treated with 20 parts water, filtered, and the solution precipitated with a large excess of sulphuric acid.

On treating the mother liquor from kermes mineral with an acid, the pentasulphide is precipitated with evolution of sulphuretted hydrogen. The mother liquor from Schlippe's salt also yields this substance on the addition of an acid (R. Bartley, Chem. Soc. Trans. 1876, 1, 748). It generally contains free sulphur.

Antimony pentasulphide is of some importance commercially, as it is used in the process of vulcanising rubber.

Antimony pentasulphide combines with alkaline sulphides, forming sulphantimonates, which as well as the sulphantimonites (which contain less sulphur) are known as ‘livers of antimony.’ Of these the sodium sulphantimonate, or *Schlippe's salt*, is the most important.

A mixture of 11 parts finely powdered antimony trisulphide, 13 crystallised sodium carbonate, 1 flowers of sulphur, 5 recently slaked lime, and 20 water, is digested at the ordinary temperature for 24 hours with frequent stirring, in a vessel which can be closed. It is then strained and washed several times with water, the solution and washings are evaporated in a porcelain or clean iron dish until a sample yields crystals on cooling; the solution is then cooled, and the resultant crystals washed with cold water and dried in the open air or in a desiccator at the ordinary temperature. The salt is more rapidly formed when the mixture is heated (Liebig, Handwörter. d. Chem. 2te Aufl. 2, 139; also Gm. 4, 384).

Oxysulphides of antimony are formed by the combination of the sulphides and oxides or by the partial oxidation of the sulphides.

Antimony crocus or saffron. Fuse together 3 parts of antimony trioxide and 1 part trisulphide, or fuse the oxide with the calculated quantity of sulphur.

The scoria from the fusion of the sulphide with carbon and alkaline carbonate in the preparation of the metal is known as crocus of antimony.

Crocus of antimony is a brownish-yellow body.

Glass of antimony. Vitrum antimonii. When antimony sulphide is fused until the necessary amount of sulphide has been converted into oxide, the whole forms a glassy mass of this compound. The best method of preparation is to roast the sulphide completely into oxide and fuse the product with $\frac{1}{20}$ part of sulphur. Its colour varies with the proportion of sulphur present from yellowish-red to hyacinth red. The best quality is of a fine red colour, and contains 8 antimonious oxide and 1 antimonious sulphide

Antimony cinnabar is an oxysulphide of a fine vermilion colour, soft and velvety, and unaltered by air or light; it is used in the preparation of oil and water colours, and in calico-printing. It is prepared by dissolving antimony oxide in hydrochloric acid, and placing the solution in a large wooden tub which is $\frac{7}{8}$ filled with calcium hyposulphite. The mixture is stirred and heated with steam to 70°, the precipitate soon subsides as a yellowish sediment which changes to a bright orange-red, and is thoroughly washed, and dried below 50°. N. Teck (Chem. Zentr. 26, 1880) prepared it from 4 parts tartar emetic, 3 tartaric acid, 18 water mixed at 60° with hyposulphite of soda and heated to 90° (Wagner), or 4 volumes antimonious chloride of sp.gr. 1·19 mixed with 10 vols. water and 10 vols. hyposulphite of 1·19 sp.gr., and heated gradually to 55° (Mattieu Blessy).

Antimony yellow (*Mérimée's yellow*). According to the method of Mérimée, a mixture of 3 parts bismuth, 24 parts antimony sulphide, and 64 parts nitre, is thrown little by little into a heated crucible, fused, powdered, washed, and dried. In this way bismuth antimonate is produced. Of this 1 part is mixed with 8 parts ammonium chloride and 128 parts litharge, and fused as before. The time occupied and the temperature used cause considerable variations in the colour. Mérimée's yellow is a fine permanent colour of good body. It is only used for the finest painting.

Naples yellow is essentially an antimonate of lead containing excess of lead oxide, but mixtures of carbonate and chromate of lead are also sold under the name. Many processes may be used for its preparation. According to Brunner, a mixture of 1 part tartar emetic, 2 parts lead nitrate, and 4 parts sodium chloride is heated, just to fusion, for 2 hours. The cooled mass is placed in water and soon falls to pieces. According to Guimet, it may be produced by heating a mixture of 1 part potassium antimonate and 2 parts red lead. It is a fine very permanent orange or yellow pigment, used in oil-painting, and, mixed usually with a lead glass, for glass and porcelain staining.

Antimony trichloride (*Butter of antimony*).

Prepared by dissolving the sulphide in strong hydrochloric acid with a small quantity of nitric acid and evaporating to dryness.

To prepare the pure chloride, the acid solution is evaporated until it just crystallises on standing in a cool place; it is then transferred to a retort and distilled until a drop of the distillate solidifies on a cold surface; the receiver is then changed, and the further distillate is pure.

It is a white, buttery, semivitreous, deliquescent solid. When pure, it is crystalline, and melts sharply at 73·2°, and boils at 223·5° (Beckmann, Zeitsch. anorg. Chem. 1906, 51, 96). It is used as a caustic in medicine, for the preparation of tartar emetic, and as a 'bronzing solution' for gun-barrels, &c. For this purpose a saturated solution is mixed with olive oil, rubbed over the warmed metal and exposed to the air until the proper colour is produced. When bronzed, the metal is polished with a burnisher or with wax, or coated with a varnish of 2 oz. shellac, 3 drachms dragon's blood, dissolved in 2 quarts of methylated spirit.

Antimony oxychloride. *Basic chloride, powder of Algaroth; pulvis Algarothi; S. Argelicus; mercurius vitæ, &c.*

Water is added to a solution of the trichloride until it is distinctly turbid, when it is filtered (the precipitate carries down any traces of sulphuretted hydrogen which may be present, and which if left would soon turn the substance yellow). Five to ten volumes of water are added, and the precipitate is washed with cold water and filtered. Its composition varies with the temperature at which it is produced and the amount of water used, varying between SbOCl and, where a very large amount of water has been used, Sb_2O_3. It is a white powder, and is principally used for the preparation of pure antimonious oxide and tartar emetic.

Antimonious oxide Sb_4O_6. *Trioxide of antimony.* If antimony is powdered and heated in a shallow dish, it eventually forms antimony tetroxide Sb_2O_4; this, together with the unchanged metal, is fused in a crucible, when the tetroxide and antimony react, forming antimonious oxide, the excess of antimony sinking to the bottom of the crucible.

For pharmaceutical purposes 20 parts of finely powdered antimony sulphide are gradually added to 100 parts hydrochloric acid containing 1 part nitric acid, and heated, gently at first, and then more strongly, until sulphuretted hydrogen ceases to be evolved. It is then boiled for an hour, enough water is added to produce a slight precipitate, which removes the last traces of sulphuretted hydrogen, and filtered into a vessel containing 1 gallon of water, precipitating the oxychloride, which is filtered and washed until it ceases to have an acid reaction; it has then become converted into the trioxide.

It is a white fusible solid, slightly soluble in water, volatile at a red heat. It becomes further oxidised to the tetroxide Sb_2O_4 on heating in air, and is then non-volatile.

In presence of alkalis it absorbs oxygen; for this reason it has been proposed to use it for reducing nitrobenzene to aniline, and in the preparation of aniline red.

It is used for the preparation of tartar emetic. When ground with linseed oil it is sometimes used as a substitute for white lead, being less injurious to the workmen and less acted upon by sulphur gases; it has, however, less 'body' and is more expensive.

Tartar emetic. *Potassium antimony tartrate. Tartarus stibiatus. Brechweinstein; spiessglanzweinstein.* $2C_4H_4K(SbO)O_6,H_2O$. Three parts antimonious oxide and 4 cream of tartar are made into a thin paste with water and digested for about half an hour, keeping the water at constant volume; 8 parts of water are then added, boiled, and filtered whilst hot. The oxychloride or oxysulphide may be substituted for the oxide, but not so satisfactorily.

Tartar emetic forms octahedral crystals, which give off a part of their water on exposure to the air. They dissolve in 14·5 parts cold and in 1·9 parts boiling water. They show an acid reaction with litmus, and have a nauseous metallic taste, 5–10 centigrams causing vomiting, and larger quantities being very poisonous.

It is used in medicine and in the preparation of pomades, &c., and also largely as a mordant in dyeing and calico-printing. Mixtures of tartar emetic for mordanting are sold containing as much as 33–59 p.c. zinc sulphate at a lower price, under the names *tartar emetic powder, tartar emetic substitute, antimony mordant*, &c. It is known that zinc acetate may partly replace the tartar emetic with advantage, but the sulphate appears to be a simple adulterant (H. Smid, Chem. Zeit. 1882, 949).

Several other compounds of antimony have been proposed for mordants instead of tartar emetic. E. Jacquet (Dingl. poly. J. 257, 168) advised the use of a mixture of basic antimony oxalate with twice its weight of ammonium oxalate. Nölting recommended the double oxalate of potash or of ammonia and antimony (Dingl. poly. J. [3] 255, 122). It is stated that the latter compounds have long been used under other names.

The use of the fluoride (which is not precipitated with excess of water) and the double fluorides of antimony and the alkalis has been patented by S. M'Lean. Watson, jun., patented a process for using trichloride with sufficient common salt to prevent the precipitation of the oxychloride (G. Watson, J. Soc. Chem. Ind. 1886, 5, 591; B. W. Gerland, J. Soc. Chem. Ind. 1884, 4, 643; and Kopp and Bruère, J. Soc. Chem. Ind. 1888, 566). A double salt of antimony fluoride and ammonium sulphate $SbF_3(NH_4)_2SO_4$, known as 'antimony salts,' is also used in dyeing, but as it attacks glass as well as metal, it should be stored and worked in wooden vessels. A good bath is 100 litres water, 400 grams antimony salts, 200 grams soda crystals, at a temperature of 50° (Frey, Bull. Soc. Md. Mulhouse, 1888, 301).

Tartar emetic as a mordant has, at the present time, been largely superseded by the double oxalate of potassium and antimony, as it is cheaper than the tartrate, and equally efficient, although it contains less antimony.

F. During has recommended the use of the double lactate of antimony and calcium, which can readily be obtained by mixing, in the dry state or in solution, alkali lactates with 'antimony salts,' or other antimonious compounds (Farber, Zeit. [20] 319). He states that at least 80 p.c. of the antimony in the solution will actually go into the cloth as mordant.

ANTIMONY SALTS. A compound of antimony fluoride with ammonium sulphate used as a mordant (*v.* ANTIMONY).

ANTINONIN. Trade name for a solution of potassium *o*-dinitrocresol used as a fungicide.

ANTIPERIOSTIN. Trade name for mercury iodocantharidate.

ANTIPYONINUM. Trade name for sodium tetraborate.

ANTIPYRIN. *Phenyldimethylpyrazolone* (*v.* PYRAZOLE).

ANTIRRHINIC ACID *v.* DIGITALIS.

ANTISEPTICS *v.* DISINFECTANTS.

ANTISEPTINE. Said to be a mixture of zinc iodide, zinc sulphate, boric acid, and thymol.

ANTISEPTOL. *Cinchonidine iodosulphate*, used as a substitute for iodoform.

ANTISPASMIN. Trade name for a combination of narceine and sodium salicylate. Used as a narcotic and sedative.

ANTITHERMIN. *Phenylhydrazone* of *lævulinic acid* $CH_3{\cdot}C(N_2H{\cdot}C_6H_5){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$ is obtained by dissolving phenylhydrazine in dilute acetic acid, adding an aqueous solution of the equivalent quantity of lævulinic (acetopropionic) acid, and crystallising the resulting yellow precipitate from alcohol (Farbw. vorm. Meister, Lucius & Brüning in Höchst a. M., G. R. P. Pat. 37737).

It forms colourless, inodorous, and tasteless scales, melts at 98°–99°, is sparingly soluble in cold water, soluble in alcohol, ether, or dilute acids. It has been employed as an antipyretic (Nicot, Chem. Zentr. 1887, 415); but, according to Stark (Chem. and Drug, 32, 651), its use in medicine is now almost abandoned, as it is too toxic for use.

ANTIVENIN *v.* SNAKE VENOM.

ANTOZONE. A supposed third modification of oxygen, assumed to be present in the fogs produced when ozone acts on reducing agents such as sodium bisulphite or hydriodic acid. According to Rothmund (Z. Elektrochem. 1917, 23, 170), the phenomenon is due to the volatile character of the reducing agent and to be directly caused by the presence of these substances in the vapour phase.

ANTWERP BROWN *v.* PIGMENTS.

ANVULA *v.* AMLAKI.

AOOD-I-BALSAM. *Balsam of Mecca* (*v.* OLEORESINS).

APATITE. A crystallised mineral, consisting of calcium phosphate in combination with fluorine, chlorine, hydroxyl, or carbonic acid, the formula being $(CaF)Ca_4(PO_4)_3$ or $3Ca_3(PO_4)_2+CaF_2$, where F may be replaced by Cl, OH, or CO_3. There are thus several chemical varieties, namely, fluor-apatite, chlor-apatite, hydroxy-apatite, carb-apatite, and oxy-apatite; the last two being also called podolite (V. Chirvinsky, 1907), and voelckerite (A. F. Rogers, 1912) respectively. On the composition of these several members of the apatite group, *see* papers by A. F. Rogers (1914) and W. T. Schaller (1912). Similarly, by partial replacement of the calcium, there are the chemical varieties mangan-apatite, cupro-apatite, and talc-apatite. In addition to these, some other trivial names are applied to varieties of crystallised apatite; for example, asparagus-stone, from Murica in Spain; moroxite, from Arendal in Norway; and francolite, from Wheal Franco, near Tavistock in Devonshire. The distinction between fluor-apatite and chlor-apatite is, however, the only one of any importance. (For the varieties of massive apatite, *v.* PHOSPHORITE.)

Apatite is often found as well-developed crystals. These belong to the hexagonal system, and are usually bounded by a six-sided prism and pyramid with the basal plane, though sometimes numerous other brilliant facets are present. The colour is commonly greenish or brownish, but sometimes sky-blue, violet, or colourless. The crystals may be transparent or opaque, and they have a vitreous to sub-resinous lustre. Sp.gr. 3·2; hardness 5 (the mineral can be scratched with a knife). Owing to its variable appearance, apatite is frequently mistaken for other minerals, and it well deserves its name, from ἀπατάω, 'to deceive.'. In determining the mineral, it is always well to test for phosphoric acid.

As microscopic crystals, apatite is present as an accessory constituent of igneous rocks of all kinds. It also occurs in metamorphic rocks and in metalliferous veins. Fine specimens are found at many localities, but only in two regions—in Norway and Canada—is crystallised apatite mined for commercial purposes. In southern Norway, particularly in the neighbourhood of Kragerö and Oedegaarden, near Bamle, extensive deposits of chlor-apatite occur in connection with gabbro (a pyroxene-felspar rock of igneous origin). Large deposits of fluor-apatite are mined in Ottawa Co., Quebec, and in Renfrew Co., Ontario; here the mineral forms beds in Laurentian gneiss, usually in association with crystalline limestone. In the iron mines at Mineville, in Essex Co., New York, small grains of apatite occur disseminated in magnetite, sometimes to the extent of 5 p.c. of the mass. Here it is separated by a magnetic process, and used for the manufacture of fertilizers.

On the Norwegian deposits, *see* J. H. L. Vogt, Die Apatit-Ganggruppe, Zeits. prakt. Geol. 1895, iii, 367, 444, 465. On the Canadian deposits, the various publications of the Canadian Geological Survey. *See* also O. Stutzer, Die wichtigsten Lagerstatten der 'Nicht-Erze,' Berlin, 1911, i. L. J. S.

APERITOL. A mixture of equal parts of valerianyl and acetylphenolphthalein, used as a laxative.

APHTHITALITE. Native sulphate of potassium and sodium, $(K,Na)_2SO_4$, containing K : Na in ratios varying from 3 : 1 to 4 : 3. It occurs sparingly as crusts and delicate platy crystallisations on Vesuvian lava; these are colourless, or often tinged with blue or green. The crystals are rhombohedral and optically uniaxial, although often simulating orthorhombic forms; and are dimorphous with the usual orthorhombic modification of potassium sulphate obtained artificially. The same mineral has been found at Rocalmuto, Sicily, and in the potash-salt deposits at Douglashall, near Westeregeln, in Prussia. Synonyms are arcanite and glaserite. L. J. S.

APHTHITE. An alloy containing 800 parts of copper, 25 of platinum, 10 of tungsten, and 170 of gold (Zeits. f. d. C. Grossgew. 4, 313).

APIGENIN *v.* FLAVONE.

APIIN. A glucoside contained in parsley and celery, forming on hydrolysis *apigenin* and a disaccharide, made up of α-glucose and a pentose, *apiose* (Vongerichten, Annalen, 1901, 121), (*v.* FLAVONE and GLUCOSIDES).

APIOL *v.* OILS, ESSENTIAL.

APIOSE *v.* CARBOHYDRATES.

APIOS TUBEROSA (Moench.), *Glycine apios* (Linn.). A leguminous plant from North America, the roots of which have been proposed as a substitute for the potato, and the young seeds for peas. Payen (Compt. rend. 28, 189) gives the following analysis of the root: Nitrogenous matters, 4·5; fatty matters, 0·8; starch, sugar, &c., 33·55; cellulose, &c., 1·3; inorganic, 2·25; water, 57·8 (*cf.* Brighetti, Chem. Zentr. 1900, i. 914).

APIUM *v.* OILS, ESSENTIAL.

APIUM PETROSELINUM (*Carum petroselinum*) *v.* FLAVONE.

APOCYNUM *v.* DIGITALIS.

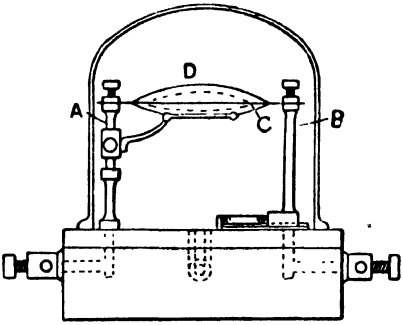
APOLLO RED *v* AZO- COLOURING MATTERS.

APOLYSIN. Trade name for monophenetidine citrate: antipyretic and analgesic.

APOMORPHINE *v.* OPIUM.

APONAL. Trade name for amy carbamate.

APOPHOROMETER, THE (Sublimation apparatus). The apophorometer consists essentially of a ribbon of thin platinum, about 6 cm. long and 4 or 5 mm. wide, stretched between two forceps, A, B, provided with binding screws so that an electric current can be sent through the platinum. One of the forceps is movable, and is acted upon by a light spring so as to keep the ribbon stretched. Beneath the ribbon is a watch-glass, C, held on a support which can be raised or lowered or turned to one side. From 5 to 30 mgrms. of the substance under examination are spread on the ribbon, the watch-glass is moved upwards into contact with the ribbon and then a second inverted watch-glass, D, is placed over the first one as a cover. A current is now passed through the ribbon and gradually increased until the sublimation temperature is attained. The temperature can be estimated with fair accuracy by means of an amperemeter. The whole apparatus may be placed under a bell-jar, if it be desired to work *in vacuô* or in an atmosphere of an inert gas. When necessary strips of thicker platinum or moulded strips of carbon may be used instead of the thin platinum ribbon. Sublimation experiments with this apparatus may with advantage be used instead of blowpipe tests for the identification of minerals, and details of experiments made with various minerals are given (Joly, Phil. Mag. 1913, 25. 301; J. Soc. Chem. Ind. 1913, 32, 509).



APOPHYLLITE *v.* CALCIUM.

APOREINE. A poisonous alkaloid found in the juice of *Papaver dubium*, m.p. 88°–89°. Forms crystalline salts, giving a bluish fluorescence in solution. The hydrochloride

$$C_{18}H_{16}NO_2,HCl,$$

forms silvery nacreous scales, subliming without decomposition in dry carbon dioxide between 220° and 240°. The neutral (normal) sulphate melts at 70°–75°, and when exposed to air and light, decomposes, forming a reddish-brown powder (Pavesi, Gazz. chim. ital. 1914, 44, 398).

APORETIN *v.* RHUBARB.

APOTHESINE. Trade name for the cinnamic ester of diethyl amino propyl alcohol. Used as a local anæsthetic. *V.* ANÆSTHETICS.

APOTURMERIC ACID *v.* TURMERIC.

APPALLAGIN. Trade name for a mercury compound of tetraiodophenolphthalien.

APPERTOL. Trade name for a preparation of sodium bisulphite. Used as a preservative and disinfectant.

APPLE. The fruit of *Pyrus Malus* (Linn.). Many varieties are known, differing greatly in size, shape, colour, and flavour.

The solid matter of apples consists largely of sugars—lævulose, sucrose and dextrose; their acidity is due to malic acid $C_2H_4O(COOH)_2$. In unripe apples starch is present—sometimes to the extent of 4 or 5 p.c., but the fully ripened fruit is devoid of starch. Cellulose forms about 1 p.c. of the weight of the ripe fruit, pentosans about 0·5 p.c., and pectose matters also about 0·5 p.c. (*cf.* Schneider, Analyst, 1912, 492). Mineral matter is usually between 0·2 and 0·3 p.c., and about half of this is potash. Apple peel contains small quantities of waxes, similar to bees-wax.

The following analyses of American Baldwin apples show the changes which occur during ripening:—

	Very green	Green	Ripe	Over-ripe
Water . .	81·33	79·81	80·36	80·30
Solids . .	18·67	20·19	19·64	19·70
Reducing sugars .	6·40	6·46	7·70	8·81
Cane sugar . .	1·63	4·05	6·81	5·26
Starch . .	4·14	3·67	0·17	none
Free malic acid .	1·14	—	0·65	0·48
Ash . . .	0·27	—	0·27	0·28

Hotter (Chem. Zentr. 1900, ii. 484) gives the following analysis of apple ash:—

K_2O	CaO	MgO	Fe_2O_3	SiO_2	SO_4	P_2O_5
51·58	4·22	3·71	1·18	1·08	2·49	10·42

Certain varieties of apples—particularly those used for cider-making—are rich in tannin, and, when the cells are broken, *e.g.* by cutting the apple or by a bruise, so as to admit air, a browning takes place—probably by the action of an oxydase upon the tannin.

Otto (Bied. Zentr. 1901, ii. 553; and 1902, 31, 107) found that the percentage of water increases during ripening on the tree, but diminishes on storing, that the starch diminishes and finally disappears, while the cellulose remains constant. The nitrogen increases during ripening on the tree, but afterwards diminishes.

The acidity diminishes during ripening, both before and after gathering.

The following figures relate to South-African apples (Ingle). The flesh and rind of the ripe fruit, the core and pips being rejected, contained :—

Variety	Koo	Reinette de Canada	Northern spy	Versfeld	Lord Wolseley
Water . .	85·08	—	82·64	87·65	84·41
Dry matter .	14·92	—	17·36	12·35	15·59
Ash . .	0·313	—	0·262	0·270	0·268
Acidity (as malic acid) .	0·47	0·65	0·48	0·71	0·47
Reducing sugars	7·44	6·87	10·26	9·43	10·85
Cane sugar .	4·63	3·68	4·77	1·36	1·58
Nitrogen .	0·046	0·094	0·058	0·057	0·043
Crude fibre .	1·33	1·24	1·26	—	0 88
Per cent. in ash:					
Potash .	54·48	—	48·52	53 30	51·58
Lime . .	2·63	—	1·95	1·82	2·70
Silica . .	1·51	—	1 58	1·25	0·90
Phosphorus pentoxide.	11·15	—	12·10	8·09	12·16
Sulphur trioxide .	2·46	—	2·67	3·13	3·10
Chlorine .	0·50	—	0·89	1·02	1·00

The proportions of lime found in these apples are apparently lower than those usually found in American apples, while the figures for phosphorus pentoxide and chlorine are higher.

Under normal conditions, the starch present in unripe apples is converted, during ripening, into sugar by the diastase present, but if the unripe apples be bruised, this change is incomplete in the bruised portion, and starch may be found in the browned tissues. According to Warcollier (Compt. rend. 1905, 141, 405), this is due to the paralysing effect upon the diastase of the tannin which escapes from the bruised cells (and which, by the action of an oxydase, gives rise to the browning), thus preventing the saccharification of the starch, upon which normal ripening depends.

According to Eoff (J. Ind. Eng. Chem. 1917, 9, 587), the preponderant sugar, in all the twenty varieties examined, was lævulose. This confirms the observations of Thompson and Whittier (Bull. 102, 1913, Delaware Coll. Agric. Expt. Stat.), and of Browne (A. 1902, ii. 371).

Apples are now dri d by artificial heat (with or without the use of sulphur dioxide, which improves the colour), and sold, either as whole fruit or as 'apple rings.' Fresh apples yield about one-seventh of their weight of the dried product. Zinc is frequently found in dried apples, probably from contact with zinc trays during the drying process. As much as 0·58 gram Zn per kilogram has been found in American dried apples. American analyses give as the average components of dried apples : 36 p.c. water, 1·4 p.c. protein, 3·0 p.c. ether extract, 57·6 p.c. carbohydrates, and 1·8 p.c. ash. The flavour, and particularly the odour, of apples can be imitated by *iso*-amyl-*iso*-valerate dissolved in spirits of wine. This constitutes the 'essence of apples' used in confectionery and perfumery.

H. I.

APPLES, ESSENCE OF, *v.* Apples.

APPLE-PULP (pomace) forms a by-product of cider manufacture, and has the following composition (8 samples) : Water (p.c.) 68·4–78·1 fat (ether extract), 0·82–1·43 ; protein, 1·03–1·82 ; crude fibre, 4·42–10·5 ; ash, 0·56–2·27 ; carbohydrates (sugar, &c.), 9·5–22·0. Most stock eat it readily, and it is a satisfactory feeding stuff if given as an adjunct to more concentrated foods. It must be given fresh, for it undergoes fermentation and putrefaction so rapidly as to be unfit for consumption in two or three days in warm weather. When dried it may be used in the manufacture of compound cakes and poultry feeds. If mixed with salt it may be preserved if tightly pressed in a silo. It usually contains from 0·2–0·6 p.c. of potash, 0·4 to 0·7 p.c. phosphoric acid, and 1·6 to 1·7 p.c. nitrogen, and makes an excellent manure, if mixed with half its weight of lime to neutralise acids (Barker and Gimingham, Journal of the Board of Agriculture, 1915, 22, 851). *See* Cider.

APPLE TREE. (*Pyrus malus*, L. ; *Pomme*, Fr. ; *Apfel*, Ger.) The wood is much used in turnery, and that of the crab tree is used by millwrights for the teeth of mortice wheels. The bark contains a tannin identical with that contained in horse-chestnut bark.

APRICOT. The fruit of *Prunus armeniaca* (Linn.).

The following analyses were made by Fresenius :—

		I. Medium size	II. Large wt. 60 grams
	Sugars . . .	1·14	1·53
Soluble	Free acid . .	0·90	0·77
	Nitrogenous matter.	0·83	0·39
	Pectins, gum, &c. .	5·93	9 28
	Ash . . .	0·82	0·75
Total soluble matter		9 62	12·72
Insoluble	Seeds (stone) .	4 30	3·22
	Skin and cellulose	0·97	0·94
	Pectose . .	0·15	1·00
	Ash . . .	(0·07)	(0·10)
Total insoluble matter, excluding ash . .		5·42	5·16
Water		84·96	82 12
		100·00	100·00

In Californian-grown apricots, Colby (Exp. Stat. Record, 1893, 4, 918) found in the whole fresh fruit, water, 85·16 ; dry matter, 14·84 ; containing nitrogen, 0·194 ; sugar, 11·10 ; ash, 0·49.

The ash was found to contain :

K_2O	Na_2O	CaO	MgO	MnO_2	P_2O_5	SO_3	SiO_2	Cl	Fe_2O_3
59·36	10·26	3·17	3·68	0·37	13·09	3 63	5·23	0·45	1·68

Californian apricots appear to contain more nitrogen than the European fruit. As many other analyses agree in giving about 11 p.c. of sugar, it is probable that some error has been made in Fresenius' figures, though they have been widely quoted.

The sugar is chiefly sucrose, with a little dextrose, and invert sugar, which becomes less when the fruit ripens (Desmoulière, Ann. Chim. anal. 1902, 7, 323). The colouring matter is probably related to carotin.

The acidity of apricots is chiefly due to malic and citric acids.

The kernels of apricot 'pits,' or stones, like those of the other members of the *Prunus* family, contain amygdalin and about 40 p.c. of a fatty oil resembling almond oil. This oil has a sp.gr. of 0·9204 at 15·5°, a pale-yellow colour, and a slight odour of almonds (Maben, Pharm. J. Trans. [3] 16, 797). More recent determinations give the following (Dieterich, Chem. Zentr. 1902, 2 [15], 943): sp.gr. at 15°C. 0·915–0·921, at 90°, 0·9010–0·9015; solidifying point, −14° to −20°; saponification value, 193·1–215·1; iodine value (Hübl), 100–108·7; refractometer value at 25°, 65·6–67·0; at 40°, 58·0; at 50°, 52·25. It can be distinguished from almond oil by Biber's reagent (fuming nitric acid, sulphuric acid and water), with which it gives a red colour, while almond oil only yields a faint yellow.

The flavour of apricots can be imitated by a mixture of *iso*amyl butyrate and *iso*amyl alcohol.

Dried apricots are prepared either by sun-drying or by artificial heat, sulphur dioxide being often employed in the latter case, in order to prevent darkening in colour. They are largely used in America and in some of the colonies. American analyses show them to contain about 32 p.c. of water, 63 p.c. of carbohydrates, 2·9 p.c. of nitrogenous matter, and 1·4 p.c. of ash.

H. I.

APRICOT, ESSENCE OF. A mixture of *iso*amyl butyrate and *iso*amyl alcohol.

APRICOT KERNEL OIL *v.* Apricot.

APYRON. Trade name for lithium acetylsalicylate.

AQUA FORTIS *v.* Nitric acid.

AQUA REGIA. *Nitromuriatic acid*; *Königswasser.* A name given by the alchemists to a mixture of nitric and hydrochloric acids, originally prepared by dissolving sal ammoniac in strong nitric acid, and used by them as a solvent for gold, sulphur, &c. Usually made by mixing 1 vol. of nitric acid with 4 vols. of hydrochloric acid. The mixture is at first colourless, but gradually—especially on heating—acquires a deep orange-yellow colour, due to the formation of nitrosyl chloride and free chlorine: $HNO_3+3HCl=NOCl+Cl_2+2H_2O$. The solvent action of aqua regia appears to be mainly due to the free chlorine.

AQUA VITAE. An alchemistic name used to denote common alcohol as obtained by distilling a liquid which has undergone vinous fermentation.

ARABIC GUM *v.* Gums.

ARABINOSE *v.* Carbohydrates.

ARACHIDIC ACID $CH_3(CH_2)_{18}COOH$ is found partly free and partly as a glyceride in earth-nut oil (from *Arachis hypogæa* (Linn.)); in butter, and in the fruit of *Nephelium lappaceum* (Heintz. Pogg. 90, 146; Grössmann, Annalen, 89, 1; Oudemans, Zeits. f. Chem. 1867, 256). It has been prepared by treating behenolic acid $C_{22}H_{40}O_2$ with fuming nitric acid (Grössmann, Ber. 1893, 644), and synthetically from aceto-acetic ester and octodecyl iodide (Schweizer. Arch. Pharm. 1884, 753): m.p. 77° (Baczewski, Monatsh. 17, 530). Solubility in 90 p.c. alcohol, 0·022 p.c. at 15°, and 0·045 p.c. at 20°.

The methyl ester melts at 54·5°, and the ethyl ester at 50°, and boils at 284°–286° under 100 m.m. pressure.

ARACHINE $C_5H_{14}ON_2$, an alkaloid occurring with choline and betaine in earth-nut (ground-nut, monkey-nut) meal (*Arachis hypogea* (Linn.)). Syrup; the aurichloride and platinichloride are crystalline. Produces somnolence in frogs and rabbits (Mooser, Landw. Versuch-Stat. 1904, 60, 321).

ARACHIS OIL is obtained from the seeds of *Arachis hypogæa* (Linn.), which are known in commerce as earth nuts, pea nuts, or monkey nuts. The cultivation of the arachis plant dates back so far in history that its origin is unknown. It is frequently assumed that the home of the arachis nut is Brazil. The plant is chiefly cultivated in the East Indies, Indo-China, Java, Japan, the West Coast of Africa, Mozambique, Madagascar, Egypt, Spain, Sicily, the United States of America, the Argentine, and in the West Indian Islands. The East Indian and West African nuts represent two distinct varieties. In commerce a distinction is made between decorticated and non-decorticated nuts. The Indian and Mozambique nuts are usually decorticated before they are shipped to Europe; as they undergo some detrimental changes on the voyage, they cannot be used for the production of best edible oil, and are mostly worked up for soap oil. The nuts coming from West Africa mostly arrive non-decorticated, and are therefore suitable for the preparation of best edible oil, the lower qualities only, derived from a second and third expression (*see* below) being used for technical purposes. The approximate composition of arachis nut, taking the average of nuts from various places of origin, is as follows: oil, 38–50 p.c.; water, 4·6–12·8 p.c.; albuminoids, 26–31 p.c.; carbohydrates, 5–19 p.c.; fibre, 1·1–4·1 p.c.; ash, 1·6–3 0 p.c.

The undecorticated nuts are shelled by special machinery and the inner red skin which surrounds the kernel is removed as completely as possible by a blast of air. The separated and cleaned kernels are then ground in the usual manner and subjected to hydraulic pressure. As the kernels contain so high a proportion of oil, the expression of the oil is carried out in two stages; frequently the meal is even expressed three times. The first expression takes place at the ordinary temperature, and yields the 'cold-drawn' oil; the second expression is carried out at a temperature of 30°–32°; and the third expression at 50°–55°.

The 'cold-drawn' oil is nearly colourless, and has a pleasant taste, recalling that of kidney beans; it is used as salad oil, and sold under the name 'huile surfine.' The oil obtained by the next expression also serves for edible purposes, in the sardine and margarine industries, or for burning; the lowest quality, which has been expressed at the highest temperature, is chiefly used for soap-making.

The arachis cakes serve as an excellent cattle food, for they contain the highest amount of proteins of all known oil cakes; moreover, these proteins are more easily digested than those of other cakes.

Their average composition is: water, 11·5;

fat, 8·8; cellulose, &c., 31·1; ash. 7·25; proteins, 41·35: nitrogen, 6·8 p.c. (Schädler).

On standing a few degrees above freezing-point, 'stearine' deposits from arachis oil. This stearine contains *arachin*, which does not settle out as a crystalline mass, so that it cannot be removed in the usual manner by expression. Hence it is necessary, in order to 'demargarinate' arachis oil, to allow it to stand for a prolonged time in the cold, when 'margarine d'arachide' settles out, so that the supernatant clear oil can be drawn off.

Amongst the solid fatty acids of arachis oil, arachidic acid and lignoceric acid have been identified. These two acids are characteristic of arachis oil, and as their proportion can be determined quantitatively, the separation and determination of 'crude arachidic acid' (*i.e.* a mixture of arachidic and lignoceric acids) furnishes an excellent means of identifying arachis oil, and estimating its proportion in mixtures with other oils. Amongst the liquid fatty acids of arachis oil, oleic acid undoubtedly predominates; in addition to it linolic acid has been identified, but the presence of hypogæic acid is doubtful, the only oxidation compound obtained from the liquid, fatty acids being a sativic acid (Klimont and Mayer, Monatsh. Chem. 1913, 34, 1195). Stearic acid does not appear to be present; the fatty acid, m p. 68°, separated by Hehner and Mitchell (Analyst, 1898, 21, 238), consisting of a mixture of lignoceric and arachidic acids (Klimont and Mayer, *l.c.*).

The sp.gr. of arachis oil is usually about 0·917–0·919 at 15°, but Sadtler (Amer. J. Pharm. 1897, 69, 490) obtained as low a value as 0·911 with oil from African nuts, whilst the oils from Indian nuts have given values of 0·9223 to 0·9256 (Crossley and Le Sueur, J. Soc. Chem. Ind., 1898, 17, 989). The usual limits for the iodine value lie between 87 and 100, but extremes of 84·4 (Schnell) and 105 (Oliveri) are on record. For its detection and estimation, *see* Evers, Analyst, 1912, 37, 487. As the iodine value of arachis oil lies so near that of olive oil, adulteration of olive oil with arachis oil takes place on the largest scale; indeed, very frequently arachis oil is entirely substituted for olive oil (as in the preparation of tinned sardines).

It is also a common adulterant of castor oil when used as a lubricant for aeroplane motors. Its presence may be detected by the turbidity temperature of an alcoholic solution of the oil, pure castor oil solutions remaining clear below −20°, whilst 1 p.c. of arachis oil causes the liquid to become turbid at a much higher temperature. Arachis oil itself is liable to be adulterated with sesame oil, which is added partly with the object of preventing solidification when the oil is exposed to a moderately low temperature. The addition may be detected by the Baudouin test (*see* Sesame Oil).

Arachis oil is chiefly expressed in the South of Europe (Marseilles and Trieste); therefore the lower qualities of this oil enter largely into the composition of the soaps of South Europe. Thus, one of the most characteristic component of the Marseilles white soap is arachis oil. The quantity of arachis nuts imported into France during the year 1907 was: arachis nuts in shells, 163,241 tons; decorticated arachis nuts, 117,404 tons. The total quantity of arachis nuts produced in the world may be taken to amount to about 350,000 tons. In 1910, 6,686,679 tons of oil seeds were imported into Marseilles, of which 34,800 tons were arachis nuts. Next to France, arachis nuts are largely imported into Trieste, Delft, and in smaller quantities to Germany (about 25,000 tons), and to the United States of America. The latter country produces about 50,000 tons per annum. The imports of arachis oil into Italy increased from 470 tons in 1908 to 5080 tons in 1910 (Molinari). J. L.

ARAGONITE. The orthorhombic form of calcium carbonate ($CaCO_3$), differing from the more common dimorphous form calcite (*q.v.*) in its greater density (sp.gr. 2·93), greater hardness (H. 3½), and in the absence of cleavage. It crystallises, together with calcite, from aqueous solutions containing carbon dioxide at temperatures above 18°, and the presence of various salts in the solution favours its growth. In nature it is deposited by thermal springs, for instance, those of Carlsbad in Bohemia, in the form of pea-like concretions, this variety of the mineral being known as *pisolite*. Another variety, called *flos-ferri* (flower of iron), is found as snow-white coralloidal forms in the iron mines of Styria. Crystals were first found embedded in red clay and gypsum in Aragon, Spain; and divergent groups of spear-like crystals have been found in an iron (hæmatite) mine in west Cumberland. Fine groups of twinned prismatic crystals are met with in the sulphur mines near Girgenti in Sicily, and in the copper mines at Herrengrund in Hungary. A variety containing about 5 p.c. of lead carbonate is called tarnowitzite from its occurrence at Tarnowitz in Silesia. L. J. S.

ARALIA BARK or *False Prickly Ash Bark*, the bark of *Aralia spinosa* (Linn.), contains a volatile oil, an amorphous bitter substance, (tannin), a grey acrid resin, and a glucoside to which the name *aralein* has been given (Lilly, Pharm. J. [3] 13, 305). By boiling aralein with dilute hydrochloric acid, *aralíretin* is obtained (Holden, Pharm. J. [3] 11, 210; Chem. Soc. Trans. 40, 105).

ARAROBA POWDER *v.* Chrysarobin.

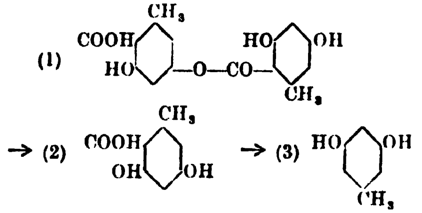
ARASINA GURGI. An impure gamboge from Camara, obtained probably from a species of Garcinia (Dymock, Pharm. J. [3] 7, 451).

ARBOL-A-BREA RESIN is obtained from *Canarium luzonicum* (Miq.), a tree belonging to the Burseraceæ, growing in the Philippines. The resin is greyish-yellow, soft, glutinous, and has a strong agreeable odour. It contains 61·29 parts of resin very soluble in alcohol; 25·00 parts of resin sparingly soluble in alcohol; 6·25 essential oil; 0·52 free acid; 0·52 bitter extractive matter; 6·42 woody and earthy impurities (Bonastre, Jour. Pharm. 10, 129). Baup has isolated four crystalline substances, *Amyrin*, *Breidin*, *Brein*, and *Bryoïdine* (Ann. Chim. Phys. [3] 31, 108).

ARBUTIN *v.* Glucosides.

ARCHIBROMIN. Trade name for monobromo*iso*valeryl glycolylurea.

ARCHIL or **ORCHIL** (*Orseille*, Fr.; *Orseille*, Ger.; *Oricello*, It.) appears in commerce in three forms: (1) as a pasty matter called *archil*; (2) as a mass of a drier character, named *persis*; and (3) as a reddish powder called *cudbear*. It is obtained from various lichens of the genus Roccella, growing on the rocky coasts of the Azores, the Canaries and Cape de Verd Isles, also of the Cape of Good Hope, Madeira, Corsica, Sardinia, &c., and from *Ochrolechia tartarea*, growing in Sweden and Norway. None of these lichens contains the colouring matters ready formed, but there are present certain colourless acids of the type of *lecanoric acid*, derivatives of orcin, into which they can be readily converted. Thus, lecanoric acid (1) gives first orsellinic acid (2) and subsequently orcin (3) according to the following scheme:—



Orcin itself, when acted upon by air and ammonia, changes into a purple substance called *orcein*, which is the name applied to the colouring matters of archil (Robiquet, Ann. Chim. Phys., [2] 47, 238).

Finely powdered orcin is placed in a thin layer under a bell jar, together with a beaker containing strong ammonia solution. As soon as the substance has become brown coloured, it is removed and exposed to air for some time. It is then dissolved in very dilute ammonia solution, reprecipitated with acetic acid, and dried. According to Gerhardt and Laurent, orcein has the composition $C_{14}H_7NO_6$ (Ann. Chim. Phys., [3] 24, 315), but more recent researches indicate that it is a mixture of substances. Liebermann, for instance (Ber. 7, 247; 8, 1649), considers that by this reaction three colouring matters are produced, having respectively the formulæ (*a*) $C_{14}H_{13}NO_4$; (*b*) $C_{14}H_{12}N_2O_3$; and (*c*) $C_{14}H_{12}N_2O_3$.

Zulkowski and Peters (Monatsh. 11, 227) allowed orcin to remain in contact with ammonia for two months, and from the product isolated three substances:—

(*a*) *Red orcein* $C_{28}H_{24}N_2O_7$, the main product, which appears to be formed according to the following equation:—

$$4C_7H_8O_2+2NH_3+6O=C_{28}H_{24}N_2O_7+7H_2O$$

It is a brown crystalline powder, soluble in alcohol with a red colour, and in alkaline solutions with a blue-violet tint.

(*b*) A crystalline yellow compound,

$$C_{21}H_{19}NO_5,$$

which is accounted for as follows:—

$$3C_7H_8O_2+NH_3+3O=C_{21}H_{19}NO_5+4H_2O$$

(*c*) An amorphous product similar to litmus.

These substances can be prepared much more rapidly by the addition of hydrogen peroxide to an ammoniacal solution of orcin.

There can be no doubt that this reaction proceeds in several stages, and that the character of the product varies according to the duration of the process. This is well known to manufacturers, who can prepare at will a blue or a red orchil. The constitution of these colouring matters has not yet been determined, but in view of the circumstances by which they are produced, it is most probable that they are members either of the *oxazine* or *oxazone* groups.

Orchil was originally prepared from the lichens by means of stale urine, which supplied the necessary ammonia, but ammonia solution is now exclusively employed. The older methods have, however, been greatly improved, and in the place of barrels the operation is carried out in large horizontal or vertical cylinders fitted with stirrers, and suitable openings for the admission of air.

In such an apparatus the weed is digested with about three times its weight of ammonia solution at 60° for from three days to one week, the admission of air being regulated according to the judgment of the manufacturer. The first product of the reaction has a blue colour, and if the process be stopped at this point, there is formed the dyeware known as *blue orchil*. On the other hand, if the action of the air and ammonia is allowed to proceed further, *red orchil* is obtained. These orchil pastes when dried and finely ground constitute the product known as *cudbear*.

Bedford (D. R. P. 57612, 1889) blows air or oxygen through the ammoniacal mixture, which, especially in the latter case, materially shortens the process. The apparatus employed is erected vertically, and by an ingenious arrangement of projecting shelves, the edges of which are turned down, a considerable quantity of the air or oxygen is entrapped, and exerts therefore a more powerful oxidising effect.

Orchil liquor is prepared by extracting the lichens with boiling water, concentrating the extract to from 8° to 10° Tw., and submitting this to the action of air and ammonia; whereas *orchil extract* is produced by the extraction of orchil paste itself.

In former times archil and cudbear were frequently adulterated with magenta, certain azo colours, extracts of logwood, brazilwood, &c.; but as the importance of these dyestuffs has now very greatly diminished, such a contamination is at the present time of rare occurrence.

Archil and its preparations are substantive colouring matters, which dye well in a neutral bath, but have the useful property of behaving nearly as well under slightly acid or slightly alkaline conditions. Even colours of considerable intensity are produced from it without difficulty, but unfortunately these are not fast to light. Wool is dyed in a neutral bath, or with addition of a trace of sulphuric acid, and silk is dyed in the presence of soap solution, acetic acid being sometimes added. Archil is not applied to cotton.

Archil was at one time employed to a large extent for 'bottoming' indigo, that is to say, the fabric was first dyed with archil and subsequently with indigo. The reverse process, known as 'topping,' has again been considerably in vogue. Cudbear and archil are also used to a limited extent in conjunction with other dyestuffs for the production of compound shades. White wines are sometimes coloured with archil, but its presence can be detected by precipitating with lead acetate and extracting with amyl alcohol, when a red colour indicates the presence of archil or magenta. The addition of a little hydrochloric acid changes the colour to yellow if magenta be present, but does not alter it if archil is the adulterant (Haas, Zeitsch. anal. Chem. 20, 869; J. Soc. Chem. Ind. 1, 119).

A. G. P.

ARCHIL REDS *v.* AZO- COLOURING MATTERS.

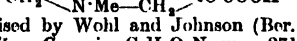
ARCHIL SUBSTITUTES *v.* AZO- COLOURING MATTERS.

ARCHIODIN. Trade name for monoiodo-*iso*valerylglycolylurea.

ARDENNITE. A mineral consisting of vanadio-silicate of aluminium and manganese, $H_{10}Mn_8Al_8V_2Si_9O_{46}$ or $H_{10}Mn_{10}Al_{10}V_2Si_{10}O_{55}$, containing 0·53-9·20 p.c. V_2O_5. The vanadium is partly replaced by arsenic (up to 9·33 p.c. As_2O_5), and in these varieties the colour is paler. It has as yet been found only at Salm-Châteaux, near Ottrez, in the Belgian Ardennes, where it occurs embedded in quartz veins in phyllites or slaty schists. It forms yellow to brown aggregates of bladed or columnar crystals; these are orthorhombic with a perfect cleavage parallel to the brachypinacoid, and good cleavages parallel to the unit prism. Sp.gr. 3·58-3·66; hardness, 6-7. It is readily fusible with intumescence before the blowpipe to a black glass; and is not attacked by hydrochloric and nitric acids, though slightly by sulphuric acid.

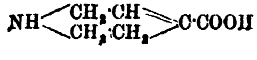
L. J. S.

ARECA NUT, *Betel nut,* is the seed of the areca palm, *Areca Catechu*, Linn., a native of the Sunda Islands, cultivated in tropical India and the Philippines. It is often chewed in the Far East together with lime and the leaves of betel pepper, and is also used as a vermifuge. In America and Europe it is used in veterinary practice, against tape worm. Arecoline hydrobromide, m.p. 170°, is employed for this purpose, and is official in the German Pharmacopœia. The nuts contain six alkaloids, all more or less closely related: *Arecoline*, $C_8H_{13}O_2N$, the principal alkaloid (0·1 p.c.) is a strongly alkaline liquid, b.p. 220°, and highly toxic (Meier, Biochem. Zeit. 1907, 2, 415). It is the methyl ester of *Arecaidine* $C_7H_{11}O_2N,H_2O$, m.p. 222°–223°, which is non-toxic and identical with Δ^3-tetrahydronicotinic acid



$$CH_2{<}\begin{matrix}CH_2\text{—}CH\\N{\cdot}Me\text{—}CH_2\end{matrix}{>}C{\cdot}COOH$$

synthesised by Wohl and Johnson (Ber. 1907, 40, 4721). *Guvacine* $C_6H_9O_2N$, m.p. 271–272°, is a lower homologue in which the N-methyl is replaced by hydrogen, is a tetrahydro*iso*nicotinic acid (probably Δ^3)



$$NH{<}\begin{matrix}CH_2{\cdot}CH\\CH_2{\cdot}CH_2\end{matrix}{>}C{\cdot}COOH$$

arecaine, m.p. 231°, is N-methyl guvacine, and hence the last two are both crystalline solids of neutral reaction. *Guvacoline* is guvacine methyl ether, b.p. 114°/13 mm., and an alkaline liquid which crystallises. For the constitution of these alkaloids, mostly discovered by Jahns (Ber. 1888, 21, 3404), for the properties of their salts and for earlier references, see Freudenberg (Ber. 1918, 51, 1668), who thinks that perhaps only arecoline and guvacoline occur as such in the nuts, and shows that arecaine of Jahns is identical with arecaidine. *Arecolidine*, $C_8H_{13}O_2N$, m.p. 110°, isomeric with arecoline, occurs in minute quantity in the mother liquors of technical arecoline hydrobromide, and is probably 3:4-dimethoxy 1-methyl, 1:2-dihydropyridine (Emde, Apoth. Zeit. 1915, 30 240).

G. B.

ARECAIINE, ARECADINE, ARECOLIDINE, ARECOLINE *v.* ARECA NUT.

AREOMETER *v.* HYDROMETER.

ARGAL *v.* ARGOL.

ARGALDIN. A combination of albumin-silver and hexamethylenetetramine.

ARGAN OIL. An oil obtained from the kernels of *Argania Sideroxylon* (Roem. et Schult) (ord. *Sapotaceæ*), growing in Morocco. The kernels are first roasted, ground to powder and mixed with water, when the oil separates (Pharm. J. [3] 10, 127).

ARGENTAMIN. Trade name for ethylene-diamine silver nitrate.

ARGENTAN *v.* ALUMINIUM and NICKEL.

ARGENTINE. A name given by R. Kirwan in 1794 to a variety of calcite ($CaCO_3$) occurring as small scales with a pearly white or silvery lustre.

ARGENTINE. Finely divided spongy tin, made by reducing a weak solution of tin salt (120 grams in 60 litres of water) by zinc. The tin is collected in a sieve, washed with water, and dried at a gentle heat. Used for tin-plating and also for printing upon fabrics and paper (Deut. Ind. Zeit. 23, 255; J. Soc. Chem. Ind. 7, 504).

ARGENTITE. A mineral consisting of silver sulphide Ag_2S, and occurring as cubic crystals or as compact masses. It is blackish lead-grey in colour, and perfectly sectile; surfaces cut with a knife are bright and shining. Sp.gr. 7·3. Containing 87·1 p.c. of silver, it is a valuable ore of the metal when met with in quantity, as in the Comstock lode in Nevada and in Mexico.

L. J. S.

ARGENTOL. A synthetic antiseptic, consisting of a compound of silver with quinosol, of the formula $C_9H_5N(OH)SO_3{\cdot}Ag$. Forms a yellowish powder, of a faint smell, sparingly soluble in water and alcohol (Pharm. Zeit. 1897, 42, 243).

ARGENTORAT. Trade name for a flash-powder consisting of a mixture of potassium perchlorate and aluminium, used in photography: gives very little smoke (*v.* FLASH-POWDERS).

ARGINASE. An enzyme occurring in the liver, also present in the kidney, the intestinal mucous membrane, thymus, and other organs (Kossel and Dakin, Zeitsch. physiol. Chem.

1904, 41, 321). Clementi (Atti. R. Accad. Lincei, 1914, [v.] 23, ii. 612, and *ibid.* 1916, 25, 1, 366) finds it in the kidney of mammals and in the liver of mammals, amphibia and fishes, but not in that of birds or reptiles; *see* also Edlbacher (Zeitsch. physiol. Chem. 1915, 95, 81–87; *ibid.* 1917, 100, 111); Shiga found it (Zeitsch. physiol. Chem. 1904, 42, 502) among the enzymes obtained from yeast. It is also found in various plants (Kizel, Bull. Acad. Sci. Petrograd, 1915, 1337–64). It can be extracted from the liver by water or dilute acetic acid, and is precipitated from solution by alcohol, ether, or ammonium sulphate. Arginase is a specific enzyme for the exclusive hydrolysis of *d*-arginine or of substances containing the *d*-arginine grouping, which it converts almost quantitatively into carbamide and *d*-ornithine. For the detection of arginase, *v.* Clementi (Atti R. Accad. Lincei, 1917, [v.] 26, i. 261). Creatine and other guanidine derivatives structurally similar to arginine, or guanidine itself, are incapable of hydrolysis by this enzyme (Dakin, J. Biol. Chem. 1907, 3, 435; and Clementi (Atti R. Accad. Lincei, 1915, [v.] 24, i. 483–489).

The action of arginase on arginine may be followed by titration of the arginine solution (in presence of formaldehyde) with N/5 sodium hydroxide solution, Clementi (Atti R. Accad. Lincei, 1914, [v.] 23, ii. 517–523); *see* also Sörensen (Biochem. Zeitsch. 1907, 7, 45–101).

M. A. W.

ARGININE $C_6H_{14}O_2N_4$, *a-amino-δ-guanino-n-valeric acid* $NH:C(NH_2)\cdot NH\cdot(CH_2)_3\cdot CH(NH_2)\cdot CO_2H$, first isolated by Schulze and Steiger (Ber. 1886, 19, 1177) from the etiolated germinated cotyledons of *Lupinus*, is the most widely distributed dissociation product of proteid matter, and can be obtained by hydrolysis of the proteid matter of seeds of *Lupinus luteus*, *Cucurbita pepo*, *Picea excelsa*, to the extent of 10 p.c., *Abies pectinata*, *Pinus sylvestris*, and other conifers (Schulze, Ber. 1891, 24, 276; Zeitsch. physiol. Chem. 1896, 22, 411, 435; 1897, 24, 276). According to Suzuki (Chem. Zeit. 1899, 23, 658) the arginine obtained from the seeds of conifers exists already formed, but in loose combination with the proteid material, and is also produced synthetically in the plant from ammonium salts and nitrates, either in full or diffused daylight (Bull. Coll. Agr. Tokyo Imp. Univ. 1900, 4, 25). It is found in a number of plants, generally in company with asparigine, less often with glutamine, and also when neither is present (Stieger, Zeitsch. physiol. Chem. 1913, 86, 268; Schulze, *l.c.* 81, 53). It is found in soil (Schreiner and Shorey, J. Biol. Chem. 1910, 8, 381; Schreiner, Lathrop, J. Amer. Chem. Soc. 34, 1242), and in the blood under normal conditions (Abderhalden, Zeitsch. physiol. Chem. 1913, 88, 478). For presence of arginine in hops, *see* Chapman (Chem. Soc. Trans. 1914, 105, 1899). According to Skinner (Bied. Zentr. 1913, 42, 213, from Proc. 8th Internat. Congress Applied Chem. 1912) it is produced in soil as a primary cleavage product of proteids and can take the place of nitrate in the soil. Arginine is also one of the constituents of the product of hydrolysis of proteids of animal origin, thus, horn yields 2·25 p.c.; glue, 2·60 p.c.; conglutin, 2·75 p.c.; albumen from yolk of egg, 2·3 p.c.; from white of egg, 0·8 p.c.; blood serum, 0·7 p.c.; and casein, 0·25 p.c. (Hedin, Zeitsch. physiol. Chem. 1894, 20, 186), whilst the protamines *Salmine*, *Sturine*, *Clupeine*, *Scombrine*, *Cyclopterine*, and *Crenilabrine* yield arginine as the chief product of hydrolysis (Kossel, Zeitsch. physiol. Chem. 1896, 22, 176; 1898, 25, 165; 1899, 26, 588; 1904, 40, 565; 1910, 69, 138). In cases of phosphorus-poisoning arginine is found in the urine (Wohlgemuth, Zeitsch. physiol. Chem. 1905, 44, 74), whilst the amount obtained from the liver is diminished (Wakeman, Zeitsch. physiol. Chem. 1908, 44, 335).

The cleavage of arginine in plants and animals due to enzyme action is identical with that which occurs in putrefactive processes: ornithine and carbamide are produced (Kossel and Dakin, Zeitsch. physiol. Chem. 1904, 41, 321; 1904, 42, 181; Ackermann, *ibid.* 1908, 56, 305; Kiesel, *ibid.* 1912, 75, 170, 196.)

When arginine is heated with barium hydroxide it is decomposed into ammonia, carbamide, and ornithine (*q.v.*) (*aδ-diaminovaleric acid*); cyanamide reacts with ornithine at the ordinary temperature to form arginine (Schulze and Winterstein, Zeitsch. physiol. Chem. 1898, 26, 1; Ber. 1899, 32, 3191), or with *a*-benzoylornithine to form the benzoyl derivative of arginine, and this is readily hydrolysed to arginine, which is thus proved to be *a-amino-δ-guanino-n-valeric acid* (Sörensen, Ber. 1910, 43, 643; *see* also Zeitsch. physiol. Chem. 1911–12, 76, 94).

Arginine yields a copper compound

$$Cu(C_6H_{14}O_2N_4)_2$$

Kober and Sugiura (J. Biol. Chem. 1912–13, 13, 5).

Arginine crystallises in brilliant monoclinic plates (Haushofer, Zeitsch. physiol. Chem. 1887, 11, 53); m.p. 207°–207·5° (Gulewitz, Zeitsch. physiol. Chem. 1899, 27, 178); it also crystallises with $1H_2O$ in rhombohedra (Hedin, Zeitsch. physiol. Chem. 1895, 21, 160); it dissolves readily in water, and is sparingly soluble in alcohol. Arginine contains an asymmetric carbon atom, and the dextrorotatory form is the natural product, the hydrochloride has $[a]_D + 12·5°$ in aqueous or $+25·5°$ in hydrochloric acid solution. Arginine is strongly alkaline, and its solution absorbs carbon dioxide from the air; it forms well-defined crystalline salts with acids, and compounds with certain metallic salts (Gulewitz, *l.c.*). The *nitrate* $C_6H_{14}O_2N_4,HNO_3,\frac{1}{2}H_2O$ has m.p. 126°; the *dinitrate* $C_6H_{14}O_2N_4,2HNO_3$ has m.p. 151°; the *hydrochloride* $C_6H_{14}O_2N_4,HCl,H_2O$ melts and decomposes at 209° when anhydrous; the *dl*-aurichloride $C_6H_{14}O_2N_4,2HCl,AuCl_3,\frac{1}{2}H_2O$ has m.p. 105°–115°; the *d*-arginine aurichloride $C_6H_{14}O_2N_4,2HAuCl_4,1\frac{1}{2}H_2O$ softens at 140° and melts at 160° (Weiss, Zeitsch. physiol. Chem. 1911, 72, 490); the *silver nitrate compounds* $C_6H_{14}O_2N_4,AgNO_3,\frac{1}{2}H_2O$ decomposes at 164°, and $C_6H_{14}O_2N_4,AgNO_3,HNO_3$ melts and decomposes at 180°; the *cupric nitrate compound* $2C_6H_{14}O_2N_4,Cu(NO_3)_2,3H_2O$ melts at 112°–114° or decomposes at 232°–234° when anhydrous; the *copper sulphate compound* melts at 110° or decomposes when anhydrous at 235°–238°; the *picrate* $C_6H_{14}O_2N_4$, $C_6H_3O_7N_3,2H_2O$, m.p. 205°, dissolves in 204·1 parts of water at 16°; the *picrolonate* $C_6H_{14}O_2N_4$, $C_{10}H_8O_5N_4,H_2O$, m.p. 231°, dissolves in 1124 parts of water, or 2885 parts of alcohol at the ordinary temperature (Schulze and Steiger, Ber. 1886, 19, 1177; Hedin, Zeitsch. physiol. Chem. 1894, 20, 186; Gulewitz, *ibid.* 1899, 27, 178; Steudel, *ibid.* 1903, 37, 219; Reisser, *ibid.* 1906, 49, 210). The aurichloride of a tetramethyl arginine

$$C_{10}H_{24}O_2N_4Au_2Cl_8$$

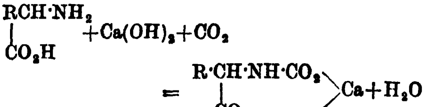
prepared by Engeland and Kutscher (Zeitsch. Biol. 1912, 59, 415) crystallises in short needles which melt 173°–175° to a clear fluid. Three methyl groups are in the side chain and one in the guanidine complex.

Certain acyl derivatives and esters of arginine have also been prepared, the *dibenzoyl derivative* $C_6H_{12}O_2N_4Bz_2$ crystallises in rhombic needles or prisms, m.p. 217·5°–218° (Gulewitz, *l.c.*), the *β-naphthalenesulphonic derivative* $C_6H_{13}O_2N_4\cdot SO_2\cdot C_{10}H_7$ is a colourless powder, m.p. 88°–89° (Reisser, *l.c.*); *diarginylarginine* is isolated as the *dipicrate* $C_{14}H_{38}O_4N_{12}(C_6H_3O_7N_3)_2,2H_2O$, m.p. 207°, from the product obtained by hydrolysing pepsin extract with hydrogen fluoride; *arginylarginine picrate* $C_{12}H_{26}O_3N_8,C_6H_3O_7N_3,2H_2O$, m.p. 213°, is similarly obtained from gelatin (Hugouenq and Morel, Compt. rend. 1909, 148, 236); *arginine methyl ester hydrochloride* has m.p. 195° (corr.) with decomposition, the *picrate* forms lemon-yellow crystals, which melt and decompose at 218° (corr.); and the *nitrate* melts at 189° (corr.) (Fischer and Suzuki, Sitzungber. K. Akad. Wiss. Berlin, 1904, 1333).

The presence of arginine assists the tryptic digestion of proteid matter and aids the emulsification of fats: this appears to be connected with its alkalinity, as sodium carbonate acts similarly (Lawroff, Zeitsch. physiol. Chem. 1899, 28, 303) When arginine (hydrochloride or carbonate) is administered as a food, it suffers complete decomposition, and 37–77 p.c. of the nitrogen so given reappears as urea (Thompson, Zeitsch. physiol. Chem. 1905, 33, 106), and the amount of arginine in the various organs shows no increase (Orglmeister, Beitr. Chem. Physiol. Path. 1905, 7, 27). Intravenous injection of arginine increases the creatine content of muscle (Thompson, Proc. Physiol. Soc. ii.–iii.; J. Physiol. 1917, 51; Jansen, Arch. Néerland. Physiol. 1, 618). Ackroyd and Hopkins (Bio-Chem. J. 1916, 10, 551–576) suggest that arginine plays a special part in purine metabolism in the animal body. Ringer, Frankel, Jonas (Bio-Chem. J. 1913, 14, 525–538), suggest that succinic acid is an intermediate compound in the katabolism of arginine.

Arginine gives the diacetyl reaction for proteids (Harden and Norris, J. Physiol. 1911, 42, 333).

Arginine is readily oxidised by hot calcium or barium permanganate yielding guanidine, γ-guaninobutyric acid and succinic acid (Bénech, Kutscher, Zeitsch. physiol. Chem. 1901, 32, 278, 413, and the estimation of the number of arginine groups in proteids is based on this reaction (Orglmeister, *l.c.*; Kutscher and Zickgraf, Sitzungsber. K. Akad. Wiss. Berlin, 1903, 28, 624), the guanidine thus obtained being isolated in the form of its sparingly soluble picrate, and either weighed as such, or the nitrogen estimated in the usual way. Another method of isolating and estimating arginine is based on Siegfried's carbamino-reaction of amino- acids (Zeitsch. physiol. Chem. 1905, 44, 85; 46, 402; 1907, 50, 171; Ber. 1906, 39, 397), whereby the barium, strontium, or calcium salt of the corresponding carbamic acid is formed when carbon dioxide is passed into a solution of the amino- acid containing excess of alkali earth hydroxide until the solution is neutral to phenolphthaleïn—



$$\begin{array}{l}\mathrm{RCH\cdot NH_2}\\ \ |\qquad\qquad +\mathrm{Ca(OH)_2}+\mathrm{CO_2}\\ \mathrm{CO_2H}\end{array} = \begin{array}{l}\mathrm{R\cdot CH\cdot NH\cdot CO_2}\\ \quad\ |\\ \quad\mathrm{CO_2}\end{array}\!\!>\mathrm{Ca}+\mathrm{H_2O}$$

The barium and strontium salts of these complex carbamic acids are much less readily soluble than the corresponding amino-acid, and afford a means of isolating the compounds (D. R. P. 188005, 1906). In order to estimate the amino- acid, the filtrate containing the calcium salt of the carbamic acid is decomposed by heating with boiled-out water into calcium carbonate, and the amino acid; the ratio $CO_2:N$ is determined by weighing the calcium carbonate thus precipitated, and estimating the nitrogen in the filtrate by Kjeldahl's method (Zeitsch. physiol. Chem. 1908, 54, 423).

Van Slyke (J. Biol. Chem. 1911, 10, 25) precipitates the arginine with phosphotungstic acid, decomposes the precipitate with barium chloride, and boils the filtrate gently with 50 p.c. potassium hydroxide for six hours; basing his estimation of arginine on the fact that it loses half of its nitrogen, in the form of ammonia, when boiled with dilute alkali.

Plimmer (Bio-Chem. J. 1916, 10, 115–119) decomposes the arginine with 20 p.c. alkali.

Wechsler (Zeitsch, physiol. Chem. 1911, 73, 138–43) dissolves the dried phosphotungstate precipitate in a mixture of acetone and water, and then decomposes it with barium hydroxide.

For the quantitative estimation of arginine, in proteins, Jansen (Chem. Weekblad, 1917, 14, 125) uses arginase to decompose the arginine and the urea thus produced is converted into ammonium carbonate by urease.

dl-Arginine is readily produced by the tryptic fermentation of fibrin, or by heating *d*-arginine nitrate at 210°–220° for 15–20 minutes (Kutscher, Zeitsch. physiol. Chem. 1901, 32, 476) or by heating *d*-arginine in 50 p.c. sulphuric acid in sealed tubes at 160°–180° for 33 hours (Reisser, Zeitsch. physiol. Chem. 1906, 49, 210); it decomposes at 210° (Cathcart, Proc. Physiol. Soc. 1905, 39); the *nitrate* $C_6H_{14}O_2N_4,HNO_3$, has m.p. 216°; the *dinitrate* $C_6H_{14}O_2N_4,2HNO_3$, m.p. 151°; the *cupric nitrate derivative* $2C_6H_{14}O_2N_4,Cu(NO_3)_2,3H_2O$, m.p. 228°–229°; the *silver nitrate derivative* $(C_6H_{14}O_2N_4,HNO_3)_2,AgNO_3$, m.p. 170°–172°; the *picrate* $C_6H_{14}O_2N_4,C_6H_3O_7N_3$, m.p. 200°–201°, is sparingly soluble

100 parts of water at 16° dissolve 0·22 part; the *picrolonate* $C_6H_{14}O_2N_4,C_{10}H_8O_5N_4$, m.p. 248°, 100 c.c. of water at 16° dissolve 0·03 grams of salt; the *β-naphthalene sulphonate* $C_6H_{12}O_2N_4\cdot SO_3\cdot C_{10}H_7,\frac{1}{2}H_2O$ has m.p. 85°–90° (Reisser, *l.c.*).

l-Arginine is formed by treating *dl*-arginine carbonate with the expressed juice of calf's liver, the ferment *arginase* present in the extract destroys the *d*-arginine, and does not attack the lævo- isomeride. With the exception of the difference in optical activity, the salts of *l*-arginine are identical with those of the dextro-isomeride, *l-arginine hydrochloride* has $[\alpha]_D^{20^\circ}$ −20·51° (Reisser, *l.c.*). M. A. W.

ARGININE. This name has also been given to an alkaloid discovered by Quiroga (J. Pharm. Chim. 1896, 16, 293) in a species of laurel (known by the natives as *viraro-mi*), growing in the east of the Argentine and west of Brazil. It forms prismatic crystals, soluble in chloroform or benzene, slightly soluble in ether, petroleum spirit, or water. Its aqueous solutions, acidified with hydrochloric acid, give a white ppt. with bromine water and a white ppt. with alkali soluble in excess. The bark and cambium contain 1·5–1·6 p.c., the wood 0·04–0·05 p.c. of the alkaloid. H. I.

ARGOFERMENT. A trade name for a form of colloidal silver.

ARGOL or ARGAL. (*Tartre brut*, Fr.; *Weinstein*, Ger.) Crude potassium bitartrate, known as red argol (*Cremore di Vinaccia*), or white argol (*Cremore di St. Artimo*), according to whether it is deposited from the red or the white grape (*v.* TARTARIC ACID).

ARGON. Sym. A or Ar. At. wt. and molec. wt. 39·88. As long ago as 1785, Cavendish (Phil. Trans. 75, 372) made experiments in order to determine whether the inert residue left after withdrawing oxygen, water, and carbon dioxide from air was homogeneous. He sparked a mixture of air and oxygen in presence of potash for the absorption of the acid produced, and removed the excess of oxygen by a solution of liver of sulphur. Only a small bubble of gas remained unabsorbed, and this did not diminish in volume on further sparking with oxygen. Cavendish concluded 'that if there is any part of the' nitrogen 'of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{120}$ part of the whole.'

Cavendish's work was overlooked for more than a century, and attention was only directed to it after the discovery, in 1894, by Lord Rayleigh (Roy. Soc. Proc. 55, 340), that the density of 'atmospheric nitrogen' was one-half per cent. higher than that of nitrogen prepared by chemical means. This result gave fresh indication of the existence of some hitherto undiscovered gas in the atmosphere, and further investigations, carried out jointly by Rayleigh and Ramsay (Phil. Trans. 186, 187), led to the isolation of a new gaseous element. The gas, which has a density of approximately 20, and which constitutes nearly 1 p.c. by volume of the atmosphere, was called *argon*, owing to its remarkable chemical inertness, in virtue of which it can be readily separated from the accom-

Argon occurs in the atmosphere to the extent of 1·3 p.c. by weight (Leduc, Compt. rend. 123, 805) and 0·933 p.c. by volume (Schloesing, Compt. rend. 121, 604; Moissan, Compt. rend. 137, 600). It also occurs in a large number of mineral waters and thermal springs (Bouchard, Compt. rend. 121, 392; Troost and Ouvrard, *ibid.* 121, 798; Moissan, *ibid.* 135, 1278; Moureu, *ibid.* 135, 1335; 142, 1155), and in the volcanic gases of Mt. Pelée (Moissan, Compt. rend. 135, 1085); it is found, moreover, in fire damp and in coal (Schloesing, Compt. rend. 123, 233). Argon has also been observed, together with helium, in the gas evolved on heating numerous minerals.

Preparation.—(i.) *By sparking air with oxygen*, the method originally employed by Cavendish (*v. supra*). The gas is preferably confined over mercury, and a small quantity of potash introduced through a curved pipette. The sparks are passed between the ends of stout platinum wires, fused through the ends of U-shaped glass tubes. These tubes are filled with mercury, and serve to establish electrical connection with the secondary terminals of a Ruhmkorff coil capable of giving a 6-inch spark through air when worked by four lead accumulators. The sparking is usually continued for several hours after contraction has ceased; the excess of oxygen is then absorbed by phosphorus (Rayleigh and Ramsay, *l.c.*; Rayleigh, Chem. Soc. Proc. 13, 181; Becker, Z. Elek. 9, 600). To save time, it is customary to prepare by method (ii.) a gas consisting mainly of argon, and to employ the method of sparking only to remove the last traces of active gases.

(ii.) *From 'atmospheric nitrogen,' the nitrogen being absorbed by a metal.* In their original investigation, Rayleigh and Ramsay separated argon from nitrogen by continuously circulating the mixture over red-hot magnesium shavings, whereby the nitrogen was absorbed, forming magnesium nitride (*cf.* Ramsay and Travers, Roy. Soc. Proc. 64, 183). This method is no longer used; a dry mixture of pure lime (5 parts) and magnesium dust (3 parts), introduced by Maquenne, is employed instead, which, when heated to redness, produces metallic calcium and absorbs nitrogen with great rapidity. By passing atmospheric nitrogen over this red-hot mixture, and leading the residual gas over metallic calcium heated to dull redness, complete absorption of the nitrogen is readily effected (Moissan and Rigaut, Compt. rend. 137, 773). Metallic lithium has also been employed for the same purpose (Guntz, Compt. rend. 120, 777; 123, 995).

(iii.) The readiest means of preparing argon in quantity consists in leading air slowly over a mixture of calcium carbide (90 p.c.) and calcium chloride (10 p.c.) heated to 800°, the mixture having previously been heated under diminished pressure to drive off any volatile matter. Both oxygen and nitrogen are absorbed by the mixture. The issuing gas is led over hot copper oxide to burn any hydrogen, hydrocarbons, and carbon monoxide present, and the water vapour and carbon dioxide removed. Using 7 kilos. of carbide, 11 litres of argon may

Ber. 41, 2017). The cyanamide process is used in America as a means of producing argon in quantity. Nitrogen obtained from the air by the copper process is repeatedly passed through the cyanamide furnaces until concentrated argon remains. It is employed in the electric lamp industry, *cf.* Bodenstein and Wachenheim, (Ber. 1918, 51, 265).

The gas prepared by the above methods contains traces of the other inert gases *neon*, *krypton*, and *xenon*, from which it is separated by fractional condensation and evaporation (Ramsay and Travers, Roy. Soc. Proc. 67, 329; Liveing and Dewar, Roy. Soc. Proc. 68, 389). The total quantity of these gases present is, however, only 0·25 p.c., and 85 p.c. of this impurity is neon.

The commercial oxygen made from liquid air contains about 3 p.c. of argon (Claude; Morey). The liquid mixture is then distilled; the oxygen condenses and the argon passes on. There is obtained a gaseous mixture containing 75–80 p.c. of argon and 1–2 p.c. of nitrogen; the remainder being oxygen, which may be removed by combustion with hydrogen.

Argon may be obtained by passing cooled compressed air downwards through a rectifying column and bath of boiling oxygen at the base. The liquid air flows over to the higher part of the column, the interior of which consists of an inner chamber with draw-off cocks at different levels. In this the mixture is separated into purer oxygen, and a rich argon mixture, which can be used for electric lamps (Eng. Pat. 101860, 1916). Fonda and General Electric Co. (U.S. Pat 1211125, 1917) produce a liquid with 94 p.c. oxygen and 4 p.c. argon, and fractionate it on the counter-current principle in such a manner that argon is removed at the top and oxygen at the bottom of the apparatus (Reports of the Progress of Appl. Chem. 1917, 11, 201).

Argon is a colourless gas, condensing to a colourless liquid, boiling at 86·9° abs. (–186 1°–186·9°/760 mm.) (F. Fischer and Froboese, Ber. 1911, 44, 92), at which temperature its density is 1·4046 (Baly. and Donnan, Chem. Soc. Trans. 81, 914). A normal litre weighs 1·78376 at 0°, and 760 mm. (Schultze, Ann. Physik. 1915 [iv.], 48, 269), coefficient of dilatation $\beta=3669\cdot10^{6}$ (8°–32°). Its m.p. is 83·4° abs. (–189·6°), its critical temperature is 155·6° abs. (–117·4°–122·44°) (Crommelin), and its critical pressure is 52·9 atmos. (Ramsay and Travers, Roy. Soc. Proc. 67, 329).

The vapour pressures of liquid argon are represented by the formula $\log p=4\cdot85033-634\cdot391T+30769\cdot09T^{2}-1076464T^{3}$. For solid argon the observations are best expressed by the formula $\log p=A/T+BT+D\log T+C$ in which $A=+9034\cdot32$, $B=-1\cdot42112$, $C=-1014\cdot0278$, and $D=+533\cdot0275$. The molecular latent heat increases from 12·92 at –125·49° to 24 01° at –140·80°, and 35·00 (cal.) at –183·06° (Crommelin, Proc. K. Akad. Wetensch. Amsterdam, 1913, 16, 477; 1914, 17, 275).

Argon is more soluble in water than nitrogen, the absorption coefficient being 0·02561, at 1°, and falling regularly to 0·02567 at 50° (Estreicher, Zeitsch. phys. Chem. 31, 176); these figures may, however, be in error by 5 p.c. (*v.* Fox, Chem. News, 99, 250). The refractive index of the gas for sodium light at N.T.P. is 1·0002837 (Burton, Roy. Soc. Proc. 1908, 80, 390); its thermal conductivity is 0·00003894 (Schwaize, Pogg. Ann. 11, (iv.) 303); and its molecular specific heat at constant volume is 2·977 cals. (Pier, Z. Elek. 15, 536; Heuse Ann. de Physik, 1919, 59, 86). Its coefficient of expansion is 0·003668 (Kuenen and Randall, Roy, Soc. Proc. 59, 60). Argon passes through rubber more quickly than nitrogen (Rayleigh, Phil. Mag. 49, (v.) 220) or carbon dioxide (Kistiakowski, J. Russ. Chem. Soc. 30, 576), and does not pass through heated platinum or palladium; it is diamagnetic (Tanzler, Pogg. Ann. 24, (iv.) 931). (For its rate of effusion, *v.* Donnan (Phil. Mag. 49, (v.) 423).)

The density of argon has been determined by several observers, with the following results: (O=16); 19·940 (Rayleigh, Roy. Soc. Proc. 59, 201), 19·941 (Ramsay, Phil Trans. 186, 238); 19·945 (Fischer and Hahnel, Ber. 43, 1435). Argon is a member of the group of inert gases, and up to the present all attempts to combine it with other elements have failed (Rayleigh and Ramsay, *l.c.*; but *cf.* Cooke, Zeitsch. physikal. Chem. 55, 537).

Atomic and molecular weight. The molecular weight, 39·88, follows from the density determinations just cited; but the atomic weight cannot be determined in the usual manner, since argon forms no compounds with other elements. The ratio of the specific heat at constant pressure to the specific heat at constant volume is 1·644 (Rayleigh and Ramsay, *l.c.*), and this result, from analogy with the case of mercury vapour and by comparison with the ratio 1·666 theoretically required for a monatomic gas according to the kinetic theory, is regarded as proof that argon is monatomic. Its atomic weight is therefore 39·88, 39·91±0 01 (Leduc, Ann. Phys. 1918, [ix.] 9, 5), coefficient of departure from Boyle's Law 10·2, 10^{-6} between 1 and 5 atmos. mol. vol. 0·999 at 0° and 760 mm.

Spectrum. This is extremely characteristic, and has been carefully examined by Crookes (Phil. Trans. 186, 243), Kayser (Chem. News, 72, 99), Eder and Valenta (Monatsh. 16, 893; 17, 50), and by Trowbridge and Richards (Phil, Mag. 43, (5) 77; Stahl (Zeitsch. wiss. Photochem. 1911, 9, 302); Stead (Proc. Camb. Phil. Soc. 1912, 16, 607). The most prominent lines are two in the red, having wave lengths of 6965·6 and 7056 4, a yellow line (6038·4), two green lines (5610 and 4702), and a violet line (4200).

ARGONIN. Silver casein.

ARGULAN. Trade name for the mercury compound of dimethylphenylpyrazolene sulphamine.

ARGYRODITE. A sulpho-germaniate of silver, being the mineral in which the element *germanium* was discovered in 1886. It had, however, been mentioned by A. Breithaupt in 1823, under the name *Plusinglanz.* These occurrences in the Himmelsfürst silver-mine at Freiberg, Saxony, show only botryoidal crusts with a minutely crystallised surface. Later, the mineral was found as distinct, though small, cubic crystals in Bolivia, analysis of which proved the formula to be Ag_8GeS_6 (S. L. Penfield, 1893 and 1894). More recently, cubic crystals of larger size (3–5 cm. across; sp.gr. 6·235) from Colquechaca, Bolivia, have been described and analysed (V. M. Goldschmidt, 1908). At this locality the mineral appears to be not uncommon, and no doubt large quantities of it have been smelted for silver. In external appearance it is not unlike argentite, but is less sectile than this.

In the Bolivian mineral the germanium may be replaced isomorphously by tin, giving the species *canfieldite* Ag_8SnS_6 (Penfield, 1894). Intermediate members of this series, or stanniferous argyrodite, also occur (Prior and Spencer, 1898). L. J. S.

ARGYROL. Syn. for silver-vitellin.

ARHEOL. Trade name for santabol.

ARHOIN. Trade name for an addition product of diphenylamine and ethylthymylbenzoate.

ARIBINE $C_{23}H_{20}N_4,8H_2O$, m.p. 229° (anhydr.) is a crystalline diacid ditertiary alkaloid from the bark of *Arariba rubra*, a Brazilian tree. The bark is used for dying wool red (Reith and Wohler, Annalen, 1861, 120, 274). Aribine is one of the very few solid alkaloids free from oxygen, and sublimes on careful heating.

ARISTINIC ACID $C_{18}H_{13}O_7N$, greenish-yellow needles, m.p. 275° (decomp.). Occurs with *aristidinic acid* $C_{18}H_{13}O_7N$, and *aristolic acid* $C_{15}H_{11}O_7N$, in *Aristolochia argentina* (Griseb.) (Hesse, Arch. Pharm. 1895, 233, 684).

ARISTOCHIN or **ARISTOQUINININE.** Trade name for di-quinine carbonate $CO(O\,C_{20}H_{23}N_2O)$.

ARISTOL. Dithymol di-iodide used as an iodoform substitute. *V.* IODOFORM.

ARISTOLOCHINE $C_{17}H_{11}O_7N$ (or $C_{32}H_{22}O_{13}N_2$?), orange-yellow needles, decomposing at 215°. Occurs in *Aristolochia Clematitis* (Linn.) and *A. rotunda* (Linn.). It is a weakly acid base (Pohl, Arch. expt. Path. Pharm. 1891, 29, 282). According to Hesse (Arch. Pharm. 1895, 233, 684) aristolochine is a homologue of aristolic acid (*see* under *Aristinic acid*). The alkaloid is highly toxic. G. B.

ARJUN WAX *v.* WAXES.

ARMENIAN BOLE *v.* PIGMENTS.

ARNATTO *v.* ANNATTO.

ARNICA *v.* RESINS.

ARNICA YELLOW *v.* AZO- COLOURING MATTERS.

ARNOTTO *v.* ANNATTO.

AROMATIC VINEGAR *v.* ACETIC ACID.

ARRACK. (*Arack* and *Rack*, Fr.; *Arrack: Reisbranntwein*, Ger.) The term 'araq' or 'arak' was applied by the Arabs to distilled spirits generally, but it is now usually restricted to the spirituous liquor obtained by distillation of the fermented juice of the coco-nut palm (toddy or palm wine), or from rice, or from a mixture of both. Arrack is also made from the succulent flowers of the Bassia genus of trees and from other vegetable products, and is manufactured not only in the East, but also in the West Indies.

Where rice is used, it is steeped in water in large vats and agitated cautiously (so as not to damage the grains, which would interfere with the subsequent fermentation) until about half the rice has begun to germinate. The water is then run off from below, and toddy or molasses or a mixture of these is added to the rice. The whole is allowed to ferment, and the mixture is then distilled.

This method, which is said to produce the best quality of arrack, obtains at Batavia and in Jamaica, but in India arrack is frequently made from toddy alone.

The best qualities of arrack are agreeable to the taste and wholesome, which cannot be said of the commoner kind made from rice alone, in some parts of India and China. This has a somewhat nauseous odour and taste, due to a volatile oil which distils from the rice, and is narcotic and very unwholesome. Its intoxicating effect is frequently increased by the addition of hemp leaves, poppy heads, stramonium juice, &c.

A large amount of revenue is obtained from the manufacture of arrack in Siam and Ceylon, and the latter exports a considerable quantity to the United Kingdom, where it is used as a valuable ingredient in making *punch*.

An imitation arrack is sometimes made by flavouring rum with flowers of benjamin or benzoic acid. J. C.

ARRHENAL. Disodium methylarsinate. *See* ARSENICALS, ORGANIC.

ARROPE. Sherry boiled to a syrup used for colouring other wines.

ARROWROOT. The starch obtained from the rhizomes of *Maranta arundinacea*, grown in the West Indies. The starch prepared from other roots is often known locally as arrowroot; *e.g.* in Queensland, where the tubers of *Canna edulis* supply such a product.

The composition of the roots of true arrowroot grown in Jamaica is:

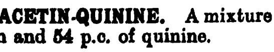
Water	Starch	Dextrin and sugar	Crude fibre	Ether extract	Proteid	Ash
63·4	27·8	2·1	3·9	0·2	1·6	0·9

(Leuscher, Zeit. öffentl. Chem. 1902, 8, 23.)

Commercial arrowroot contains from 83·5 to 86·9 p.c. starch, 11·0 to 15 p.c. water, proteins from 0·4 to 1·4 p.c., with small quantities (*circa* 0·3 p.c.) of ash, cellulose, and fat.

(For a series of analyses of arrowroots from various sources, *see* Ballard, Jour. Pharm. 1903, 17, [10] 476.) H. I.

ARSACETIN. The sodium salt of acetyl-*p*-aminophenyl arsenic acid—



$$CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{=}{\cdot}As\begin{cases}-OH\\=O\\-ONa\end{cases}$$

(*v.* ARSENICALS, ORGANIC).

ARSACETIN-QUININE. A mixture of 43 p.c. arsacetin and 54 p.c. of quinine.

ARSALYT. Bismethylaminotetra-aminoarsenobenzene.

ARSAMIN. Trade name for sodium arsanilate. Used in the treatment of sleeping sickness and other diseases of protozoal origin.

ARSAN. Glidin preparation of silver.

ARSANILIC ACID. p-Aminophenylarsinic acid. *See* ARSENICALS, ORGANIC.

ARSENIC. (*Arsenic*, Fr.; *Arsenic, Arsen*, Ger.) *Schwerbenkobalt, Fliegengift, Näpfchenkobalt Arsenicum. Regulus Arsenici.* Symbol, As; at. wt. 74·96.

Occurrence.—Arsenic, in small quantities, is one of the most widely distributed elements; it is found in mineral and other waters, in seawater and in sea-weeds, in coal smoke, in most pyretic minerals, and in a large number of ores.

In England it occurs principally with *tin ore*, and on the Continent in *mispickel.* Arsenic occurs native (usually associated with iron, cobalt, nickel, antimony, and silver) in crystalline rocks and in the older schists, generally in reniform and stalactitic masses, often mammillated; it also occurs occasionally in rhombohedral crystals. At Zimeoff in Siberia, large masses are found; it occurs in the silver-mines of Freiberg, Annaberg, Marienberg, and Schneeberg in Saxony; at Joachimsthal in Bohemia, Andreasberg in the Hartz, Kapnik in Transylvania, Orawitza in the Banat, Kongsberg in Norway, St. Marie-aux-Mines in Alsace, in Borneo, and in the United States.

As *arsenide* it occurs combined with iron in two forms $FeAs_2$ and Fe_2As_4; with nickel as *Kupfernickel* NiAs and $NiAs_2$; with cobalt as *tin white cobalt*, $CoAs_2$. With antimony it occurs as *arsenical antimony*, at Przibram in Bohemia; with blende, antimony and spathic iron, at Allemont, at Schladming in Styria and Andreasberg in the Hartz.

Arsenic is generally present in native sulphur. Combined with sulphur it occurs as *realgar* or *ruby sulphur* As_2S_2 in Hungary, Saxony, Switzerland, and China; and as *orpiment* As_2S_3 in Hungary and the Hartz.

With *sulphur* and *iron* it occurs as *mispickel, arsenical pyrites*, or *white mundic* FeS_2FeAs_2; with sulphur and cobalt in *cobalt glance* CoS_2CoAs_2; in *nickel glance* NiS_2NiAs_2, and in a number of other ores, being obtained as a secondary product in the roasting of *tin* and *copper ores, copper nickel, arsenical fahl ores, smaltine, cobalt* and *nickel glance*, &c.

With *oxygen*, arsenic occurs as *arsenolite* or *arsenite* As_4O_6, usually as a crust on other arsenical minerals, being formed by their decomposition. With *oxygen* and *cobalt*, it forms *cobalt bloom* or *arsenate of cobalt*; it also occurs as arsenates of iron, copper, and lead.

Preparation.—Metallic arsenic is used only to a small extent in commerce. It is usually prepared from native arsenic, arsenical iron, or mispickel, the latter being the only mineral used to any extent in England. The mineral used is heated in earthenware retorts or tubes laid horizontally in a long furnace. Great care is required in manufacturing the retorts; a mixture of 1 part fresh clay and 2 parts bricks or old retorts powdered, is made into the proper form, coated with a mixture of blood, loam, forge-scales and alum to produce the glaze, and burned. They are very strong and heat-resisting, and quite impervious to the vapour of arsenic. A piece of thin iron sheet is rolled and inserted into the mouth of the retort, and an earthen receiver luted on. On distilling, most of the arsenic condenses in the iron as a nearly white, coherent, internally crystalline mass, and is detached on cooling by unrolling the iron. If required, the arsenic is purified by redistillation.

At Altenberg in Silesia, arsenious oxide is heated with charcoal in an earthen crucible covered with an inverted crucible or conical iron cap. This method is more economical and productive than the one above described, but the metal is grey and pulverulent, and always contains arsenious acid.

It may also be prepared by heating the sulphides with charcoal and sodium carbonate or potassium cyanide.

Properties.—Arsenic is a very brittle steel-grey metalline mass of sp.gr. 5·62 to 5·96, of brilliant lustre, crystallising in rhombohedra, isomorphous with metallic antimony. It is a good conductor of electricity, and is odourless and tasteless.

It is volatile at temperatures above 100°, and is rapidly vaporised at a dull-red heat. At the ordinary pressure it volatilises without previous fusion, the vapour being yellow and of a garlic smell, but when heated under pressure it melts at 850°(±10°) (817°, Gouban, Compt. rend. 1914, 158, 121; 852° Heike, Intern. Zeitsch. Metallographie, 1914, 6, 49). Joubert states that above 200° its vapour is phosphorescent (Compt. rend. 78, 1853).

When the vapour is condensed at a temperature but little below the volatilising point, *i.e.* when condensed in an atmosphere of arsenic, a nearly white compact mass of strongly metallic lustre is produced which scarcely oxidises in the air even when heated to 80°. When it is deposited on a colder surface or in an atmosphere other than arsenic, it forms less dense, dark-grey crystals which readily oxidise in the air even in the cold, and especially on heating.

Ludwig (Arch. Pharm. [2] 97, 23) has obtained arsenic (?) with a perfectly bright surface resembling freshly granulated zinc, and of the low density 5·395, by distilling in a tube with a small quantity of iodine.

Bettendorf (Annalen, 144, 110) has obtained a specular, amorphous, vitreous arsenic of sp.gr. 4·69-4·716 by subliming arsenic in a stream of hydrogen and condensing it at 210°–220°. At 360° it is converted into the crystalline form with the evolution of considerable heat, and when heated suddenly it hisses and gives off vapour whilst transforming.

There is a yellow form of arsenic of sp.gr. 2·03 crystallising in the regular system. These various modifications are regarded as due to differences in molecular complexity, or as arising from the same quantity of matter distributed throughout a varying space (Kohlschütter, Frank and Ehlers, Annalen, 1913, 400, 268; Durrant, Chem. Soc. Trans. 1919, 134). Colloidal arsenic is known and would appear to be soluble in carbon disulphide.

When heated in air it absorbs oxygen, burning with a bluish flame and forming arsenious oxide. In pure water it is unaltered, but when exposed to air it forms a grey powder supposed by some to be a suboxide, but probably a mixture of metallic arsenic and arsenious oxide; this powder is sold as 'fly-powder.' When powdered and thrown into chlorine, it ignites, forming the trichloride; with the aid of heat it combines with bromine, iodine, and sulphur. Hydrochloric acid has but little action on arsenic, but it is rapidly dissolved by nitric acid, *aqua regia*, or by a mixture of hydrochloric acid and potassium chlorate.

When deflagrated with nitre it forms potassium arsenate.

Arsenic is a constituent of many alloys; it is used for bronzing brass and for the manufacture of opal glass.

(For the distribution of arsenic in commercial products, *v. Arsenious oxide.*)

Detection. — Arsenical compounds, when heated on charcoal, give off the characteristic garlic odour and white fumes of the oxide, with a white incrustation on the charcoal some distance from the assay. Metallic arsenic, and many arsenical minerals, such as mispickel, when heated in a tube closed at one end, form a blackish, shining metallic ring on the cooler portion of the tube; if heated in a tube open at both ends, the arsenic is oxidised, and condenses in a ring of white octahedral crystals, their shape being plainly visible under a lens. On cutting off the closed end of the tube containing the metallic mirror, and heating, it is also converted into the white ring higher up the tube. The white crystals dissolve in boiling water, and the solution shows the usual tests for arsenic. Antimony under like circumstances would produce a white ring, which, however, is not crystalline, and is not soluble in water. Oxides of arsenic require to be mixed with charcoal before they produce the black mirror. Sulphides require the addition of alkaline carbonate or potassium cyanide, or they may be heated with baryta alone (Brame).

White arsenic when heated with about 3 parts of sodium acetate, gives the offensive smell of kakodyl.

In solution the reactions of the two series of compounds, the arsenious and the arsenic, differ considerably; generally speaking, arsenic compounds may be converted into the arsenious form by heating with sulphurous acid or with a sulphite.

Reinsch's test. If a piece of clean metallic copper is immersed in a solution of arsenious acid or an arsenious compound acidulated with pure hydrochloric acid, it is coated with a grey film, which is probably an arsenide of copper. The action proceeds better at the boiling temperature. The acid must first be tested in the same manner to ensure the absence of arsenic, which is always present in the commercial acid. The metal is washed, dried gently and heated in a tube, when the arsenic becomes oxidised and forms a *crystalline ring* on the colder part of the tube. A film due to antimony, as mentioned before, would not produce a crystalline ring.

This method is used in testing for and removing arsenic from hydrochloric acid, and in toxicology; by it 1 part of arsenic can be detected in 250,000 parts of solution.

It is not so delicate as Marsh's or the electrolytic method.

When hydrogen is generated in a liquid containing an arsenious compound, the arsenic combines with it and passes off as the gaseous hydride; many very delicate tests are based on this reaction.

(1) *Fleitmann's test.* The solution is mixed with excess of caustic potash, a piece of *pure* zinc, or of magnesium, or aluminium foil inserted, and the solution heated. A piece of filter paper moistened with silver nitrate is held over the mouth of the tube. In presence of arsenic, arseniuretted hydrogen is produced and reduces the silver on the paper forming a greyish or purplish colour. Antimony is not evolved in this test. Fleitmann's test is therefore a ready means of finding arsenic in presence of antimony; it is not, however, so delicate as Reinsch's, Marsh's, or the electrolytic method. Or instead of silver nitrate the paper (preferably Michallet drawing paper), cut into strips, may be soaked in a 1 p.c. solution of mercuric chloride and, after drying, exposed to the gas, when the arseniuretted hydrogen produces a stain.

Gutzeit test. For a convenient form of apparatus for making this test, adapted to works practice, *see* Hollins, Jour. Soc. Chem. Ind. 1917, 36, 576.

(2) *Marsh's test.* This or Reinsch's test is usually used in toxicology. The solution is acidulated with pure hydrochloric acid and introduced into an apparatus in which hydrogen is generated by means of pure sulphuric acid and zinc. Arsenic hydride is formed and is passed through a narrow glass tube, which is heated at one spot by a lamp; the arseniuretted hydrogen as it passes over the heated portion is decomposed with the precipitation of arsenic as a black ring. In testing for very small quantities of arsenic, the action should be continued for about an hour. A blank experiment should always be performed in the same manner to ensure the purity of the zinc and acid. It is essential not only to obtain zinc and acid which are free from traces of arsenic, but also to see that the zinc used is 'sensitive,' and will permit all the arsenic in the solution to be evolved as arseniuretted hydrogen. The presence in the solution of certain metals—notably iron—is liable to retard, or entirely prevent, the evolution of arseniuretted hydrogen. (On the presence of arsenic in glass as a source of error in the detection of arsenic, *v.* W. Fresenius, Zeitsch. anal. Chem. 22, 397; Ber. 17, 2938.) Instead of heating the tube, the gas may be ignited at the mouth of the tube, and the flame caused to impinge on a cold surface of porcelain, or preferably of platinum foil. The arsenic film may be distinguished from that produced by antimony as follows:—

(1) The arsenic film is quickly evaporated, while that of antimony only slowly disappears. Helling (Das Microscop in der Toxicologie) recommends that small spots be heated and the vapour received on a slip of glass, when, under the microscope, the octahedral crystals due to arsenic are visible.

(2) The arsenic film quickly dissolves in a freshly prepared solution of sodium hypochlorite; the antimony film is very slowly soluble. Old hypochlorite solutions contain chlorite which dissolves the antimony mirror.

(3) The antimony film dissolves quickly in yellow ammonium sulphide, leaving an orange-yellow residue on evaporation; the arsenic film dissolves very slowly.

Magnesium may also be employed in place of zinc, and E. Davy and Al. Jandousch use an amalgam of 1 part sodium in 8 parts mercury, with or without acid.

The presence of nitrates or nitric acid interferes with this test, and the acids used should be dilute.

Bettendorf's test. A solution of stannous chloride in concentrated hydrochloric acid is mixed in a test-tube with a solution of the substance in hydrochloric acid, and heated to boiling, when a brown colouration indicates the presence of arsenic.

For the detection of small quantities of arsenic in toxicology, Billeter (Helv. Chim. Acta, 1918, 1, 475; Analyst, 1919, 51) recommends that the substance be treated with nitric and sulphuric acids to destroy organic matter, the sulphuric acid solution then distilled with the addition of sodium chloride and potassium bromide, the distillate evaporated with the addition of hypochlorous acid, and the residual solution tested in the Marsh apparatus. The distillation part of the process is essential to ensure removal of heavy metals, particularly mercury, traces of which completely mask the presence of relatively large quantities of arsenic in the Marsh apparatus. The addition of hypochlorous acid during concentration of the hydrochloric acid solution prevents loss of arsenic.

(For the detection and estimation of arsenic by electrolytical methods, *v. Arsenic* in art. ANALYSIS, ELECTRO-CHEMICAL.)

Estimation.—Arsenic is usually estimated as (1) magnesium pyro-arsenate; (2) as arsenic sulphide; (3) as metallic arsenic.

(1) For this method it is necessary that the substance should be present as an *arsenic* compound. The conversion from the arsenious to the arsenic condition may be effected by heating with nitric acid (*v.* Estimation as sulphide) or hydrochloric acid and potassium chlorate.

The acid solution, which should occupy only a small bulk, is mixed with 'magnesia mixture' and rendered *strongly* alkaline with ammonia. After standing for 24 hours, the solution is filtered, the last portions of the precipitate, which consists of ammonium magnesium arsenate, being washed entirely on to the filter paper with a little of the filtrate (the volume of this filtrate should be noted roughly). The precipitate is then washed with a mixture of 1 part strong ammonia and 3 parts water, until only a slight opalescence is produced on the addition of nitric acid and silver nitrate to a few drops of the washings. It is then dried, detached as much as possible from the filter paper, and transferred to a weighed porcelain crucible, moistened with nitric acid, dried, and ignited, at first gently, and finally to bright redness. The paper is moistened with nitric acid, dried, and ignited on the lid, and the crucible and its contents weighed. The ignited residue consists of magnesium pyro-arsenate $Mg_2As_2O_7$, and contains 48·27 p.c. of arsenic.

On account of the solubility of the ammonium magnesium arsenate, an addition should be made to the weight obtained of 0·001 gram for each 16 c.c. of filtrate obtained, not counting the washings.

(2) The arsenic for this method should be in the arsenious form. If *arsenic* compounds are present, they are preferably reduced by passing a current of sulphurous acid through the liquid, the excess of that gas being driven off by subsequent heating. Sulphuretted hydrogen is then passed through the liquid until thoroughly saturated, the liquid left to stand for some time, the excess of sulphuretted hydrogen driven off by heating, and the precipitated arsenious sulphide containing sulphur filtered off. The sulphide is dissolved in ammonia, filtered if necessary, and the arsenic estimated in the solution by one of the three following methods:—

(*a*) The solution is evaporated to dryness in a porcelain dish, then covered with an inverted funnel, and fuming nitric acid added. After the first violent action has ceased, the liquid is heated on a water-bath until the whole of the sulphur has disappeared, and only a small bulk of liquid remains; 'magnesia mixture' is then added, followed by excess of ammonia, and the process followed as already described.

(*b*) The ammoniacal solution is evaporated to dryness in a porcelain dish, and heated on a sand-bath to drive off the whole of the free sulphur and carbonise any organic matter (which is frequently present in toxicological analysis) without volatilising any of the arsenious sulphide. The residue is again dissolved in ammonia, filtered if necessary, evaporated to dryness, and gently heated in a weighed porcelain dish, and weighed as arsenious sulphide As_2S_3 (Mohr, Chem. Toxicologie, 56).

(*c*) The arsenic in the solution may be estimated by means of standard iodine solution (Champion and Pellet, Bull. Soc. chim. [2] 26, 541).

(3) For this method the arsenical mirror obtained by the Marsh-Berzelius method or the electrolytic method may be estimated by comparison with standard mirrors obtained under similar conditions to the estimation. Experience has shown that when in the preparation of standard mirrors, the quantities of arsenic used differ by amounts such as 0·002 milligram, a series of mirrors can be obtained showing differences in intensity which are sufficiently distinct and constant to be utilised for comparison.

Separation from other metals.—Certain heavy metals, if present, would be precipitated with the arsenious sulphide by means of sulphuretted hydrogen. From the sulphides of lead, bismuth, &c., the arsenious sulphide can be dissolved by digestion in ammonium sulphide. The solution would also contain antimony and tin, if present. The separation of arsenic from these two metals may be performed as follows:—

From antimony. The mixed sulphides are oxidised with *aqua regia*, as already described, and tartaric acid solution added, followed by excess of ammonium chloride and ammonia. The latter should produce no opalescence. If a precipitate is produced, a further quantity of tartaric acid or ammonium chloride must be added. The solution is then precipitated by 'magnesia mixture,' and the estimation made as before described.

From tin. A solution of oxalic acid is added to the solution in the proportion of 20 grams of oxalic acid for each gram of tin supposed to be present. The solution should be sufficiently strong for the acid to crystallise out on cooling. The liquid is heated to boiling and sulphuretted hydrogen passed through for 20 minutes. The liquid is allowed to stand for about 30 minutes, and the arsenious sulphide filtered off. It is quite free from tin.

Arsenious chloride in small quantities may be separated from other metals by distillation of the hydrochloric solution (Thorpe, Chem. Soc. Trans. 83, 971); in certain metals and alloys by distillation of the finely divided material with a suitable solution of ferric and calcium chlorides, acidified with hydrochloric acid (the materials used should be tested for arsenic). With a solution of zinc and cupric chlorides in hydrochloric acid boiling at 108° both arsenic and antimony may be separated from other metals; the arsenic is in the distillate from 108° to 115°, the antimony in the distillate from 115° to 160° (Gibb, J. Soc. Chem. Ind. xx. 3).

For the estimation of arsenic in ores, Parnell recommends the following method:—A weighed quantity of the *finely powdered* ore is heated to about 200° in a slow current of chlorine gas, the volatilised arsenious chloride being absorbed in a solution of chlorine water. After evaporation of the excess of chlorine, the arsenic may be estimated by any ordinary method. Antimony, if present in the ore, would also volatilise with the arsenic.

For technical purposes the following methods are largely used:—

A weighed portion is partially decomposed with a minimum quantity of strong nitric acid, dried and fused with sodium peroxide or a mixture of sodium carbonate and nitre. The fused mass is extracted with water and filtered. The solution of alkaline arsenate is acidified with nitric acid and boiled to effect decomposition of either peroxide or nitrite; it is next carefully neutralised and then acidified with acetic acid, and the arsenic determined by titration with a standard solution of uranium acetate. Pearce recommends separation as silver arsenate from the aqueous extract after fusion; the silver salt is dissolved in dilute nitric acid and estimated by Volhard's method. With very poor ores to the solution in nitric acid a sufficient quantity of tartaric acid is added, and the arsenic separated as magnesium ammonium arsenate. For the estimation of arsenic in organic salts ignite with sodium peroxide, reduce with hydriodic acid and titrate with iodine and starch in presence of disodium hydrogen phosphate (Morgan, Chem. Soc. Trans. 1909, 95, 1477).

Alloys of arsenic.

Arsenic combines with most metals, in many cases in atomic proportions, the alloys being then known as arsenides. Many natural arsenides occur as minerals.

The alloys may be prepared (1) by fusing the metals under a layer of borax, or in an atmosphere of some inert gas; (2) by reducing the arsenite or arsenate of the metal with potassium cyanide; and (3) in some cases—as with gold, silver, and copper—by placing arsenic in a solution of a metallic salt. W. Spring (Ber. 16, 324) has obtained crystalline alloys of arsenic with other metals by repeatedly compressing a mixture of the constituents at 6500 atmospheres.

When heated out of contact with air, arsenical alloys usually lose a portion of their arsenic; heated in air the arsenic is oxidised, a portion volatilising, and the remainder forming an arsenite or arsenate of the metal. When heated with nitre, arsenates are produced. (For a list of alloys of arsenic in atomic proportions, probably existing as arsenides, *v.* A. Descamps, Compt. rend. 86, 1022 and 1065.) Some ancient copper spear-heads from Cyprus contained 1·348 p.c. arsenic, and a bronze figure of the Ptolemaic period from Egypt contained 1·479 p.c.

The presence of arsenic generally renders an alloy more brittle, more fusible, and brighter. In Pattinson's process it tends to render the crystals smaller, and thus lengthens the time required for draining. Its alloys with iron, zinc, and tin are brittle; with gold and silver, brittle, and grey; and with lead and antimony, hard, brittle, and fusible. The addition of from 3 to 6 parts arsenic to 1000 lead (with occasionally little copper) causes the small shot in fallin down the tower to form spheres, instead c elongating, as they have otherwise a tendenc to do. The arsenic is frequently added in th proper proportions in the form of an alloy c lead and arsenic known as 'temper'; this i prepared by fusing together arsenious oxide an lead. By heating a mixture of lead and arseni to whiteness, Berthier obtained an alloy c the formula Pb_4As, any excess of arsenic beyon that corresponding to this formula being volatilised at that temperature. With copper it forms white, malleable, dense, and fusible alloys. White copper contains about 10 p.c. arsenic. Arsenic is also used in speculum metal, and is frequently present in common Britannia metal.

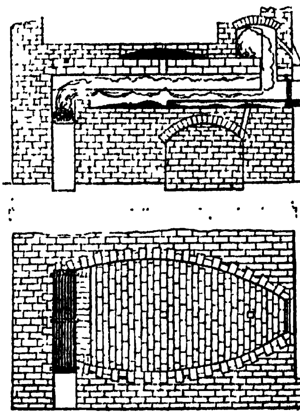


FIG. 1.

With potassium and sodium arsenic forms alloys which evolve arseniuretted hydrogen when placed in water. With platinum it forms a fusible alloy, and was formerly used to facilitate the working of that metal. It forms an amalgam As_2Hg_3 (Dumesnil, Compt. rend. 1911, 152, 868).

Arsenic trihydride. *Arsenetted or arseniuretted hydrogen. Arsine.* AsH_3. This gas is formed whenever hydrogen is liberated in a solution containing arsenious acid or an arsenite, as when zinc is introduced into an acid solution of the substance. It is a colourless, neutral, disagreeably smelling gas, slightly soluble in water, and highly poisonous, even when much diluted. At a red heat it decomposes into arsenic and hydrogen.

It can be condensed to a liquid, and forms a hydrate $AsH_3,6H_2O$ (De Forcrand).

It is evolved in the bronzing of brass with arsenic, in tinning sheet iron and frequently in the desilverisation of lead with zinc and subsequent heating of the argentiferous zinc with acid. It is a very powerful reducing agent, precipitating silver, gold, and other metals from their solutions. Methods for the quantitative estimation of arsenic are based on this property.

A solid hydride of arsenic H_2As_2 is formed by the action of an electric discharge on the trihydride in an ozoniser, or by the decomposition of sodium arsenide; or, mixed with arsenic, by the action of the trihydride on solid alkali hydroxide followed by the addition of water:

(1) $AsH_3+3KOH=K_3As+3H_2O$
(2) $2K_3As+6H_2O=As_2H_2+6KOH+2H_2$

(Reckleben and Scheiber, Zeitsch. anorg. Chem. 1911, 70, 255).

Arsenious oxide. *Arsenious acid. White arsenic. Flowers of arsenic; commonly known as 'arsenic.'* As_4O_6.

Preparation.—In Cornwall, Devon, and at Swansea, arsenious oxide is principally prepared by roasting mispickel, which occurs mixed with iron and copper pyrites, tin ore, wolfram, blende, galena, &c. These ores, if present in sufficient quantity, are separated as far as possible before roasting; tinstone by washing the finely powdered ore, and the other minerals by hand. Arsenious oxide is also largely prepared by roasting arsenical silver at Andreasberg, and from arsenical ores of nickel and cobalt.

In ores from which arsenic is produced as a principal product, the arsenical pyrites generally occur to the amount of about 12 p.c.

The ores are usually roasted in a reverberatory furnace. In a common form, the furnace bed is flat, 12–15 feet long and 7–9 feet wide in the middle; the arch is about 2 feet above the bed, and sinks gradually towards the flue, at which end there is an iron door, through which the ore is raked (Fig. 1).

From 8–15 cwt. of the stamped dried ore is introduced through a hopper over the centre of the fire-bridge and spread over the furnace bed. The heat is raised to dull redness and the ore is frequently stirred to ensure thorough oxidation of the arsenic and sulphur. In about 10 hours these have been expelled as oxides, and the arsenious oxide together with some of the sulphur collects in the flues. The spent ore is removed through an aperture in the bed, which is closed with an iron door during calcination.

Two such furnaces are sometimes built side by side, separated by a wall, and with their flues uniting. The furnace beds slope gently towards a narrow fireplace. In the first instance the ore is introduced through a number of doors on each side of the furnace. As the ore is worked downwards its place is constantly supplied by fresh ore through an opening in the roof.

Brunton's Calciner is much used in Cornwall. It is practically a reverberatory furnace with a revolving bed. The bed is of firebrick resting on a cast-iron table, and is higher at the centre than at the periphery. It is usually 8 or 10 feet in diameter; it revolves three or four times in an hour by steam or water power, about half-horse power being required. There are two furnaces on opposite sides of the bed.

The dried and finely stamped ore is introduced through a hopper over the centre of the bed. Above the bed are fixed radially three cast-iron frames in which are fastened a number of equidistant iron scrapers shaped like the coulter of a plough and placed obliquely, so that, as the bed revolves, they turn the ore over and outwards towards the periphery of the bed. It is thus thoroughly roasted, and, on reaching the edge, falls into the chamber beneath.

Oxland and Hocking's Patent Calciner (English Pat. 1868, 2950) is largely used, especially for 'rank' ores (Figs. 2 and 3). It consists of a wrought-iron cylinder, which, if 32 feet in length, is lined with sufficient firebrick to leave 4 feet clear internal diameter. Four longitudinal ribs of firebrick occur within the furnace, leaving sufficient space at the upper end for the continuous supply of the ore. The cylinder is generally mounted in an inclined position, the slope being usually ½ to 1 inch per foot, and is turned by means of a turbine or water-wheel once in 8 or 10 minutes upon friction-wheels.

The dried, finely powdered ore is introduced through an archimedean screw, or from a hopper at the upper end, and in the revolution of the tube becomes lifted to a certain height by the ribs of firebrick, and falls in a fine stream through the hot blast. In a few revolutions the ore is completely oxidised, the arsenic burning off first, and finally reaches the lower end of the tube, where it falls through a chamber beneath. A calciner of the above size will roast 6 to 7 tons of ore in 24 hours. In this furnace the amount of air required is minimised, thus rendering the condensation less difficult. The amount of fuel used is also small (*v.* further, Henderson, Proc. Roy. Inst. Mech. Engineers, 1873).

A modification of this furnace was patented by R. & C. Oxland (Eng. Pat. 7285, 1885). It is so arranged that the products pass into the condensing chambers unmixed with other gases. At the lower end of the rotating tube is a cast-iron prolongation, heated externally by a grate and a system of flues surrounding it. At the end of the prolongation is a door for removing

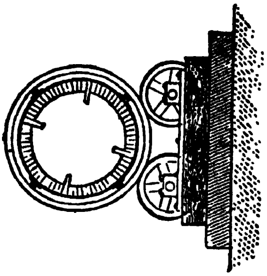


FIG. 3.

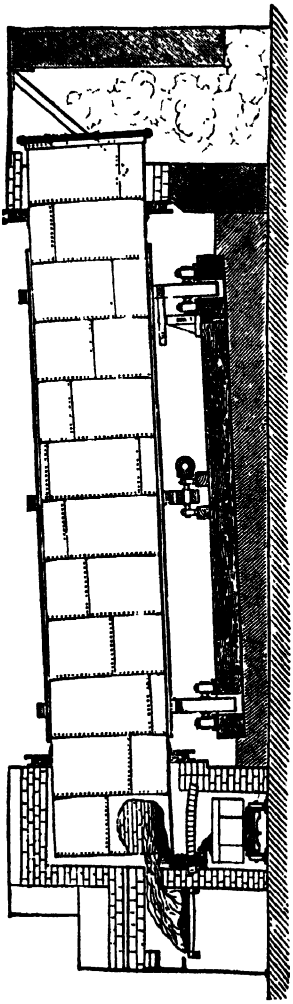


FIG. 2.

the calcined products and a regulator for admitting the required amount of air.

The practice in the West of England is to use these types of furnace for specific purposes, the Oxland type for calcination of selected mispickel ore, usually the size of gravel; the Brunton and reverberatory type for the calcination of concentrate produced in the washing of the tin ores. The small works favour the reverberatory furnace, and the large works the Brunton. More recently the Merton furnace has been installed by a few mines. It is an improved form of reverberatory furnace with several hearths in tiers and mechanical rakes for transferring the material progressively from one hearth to another.

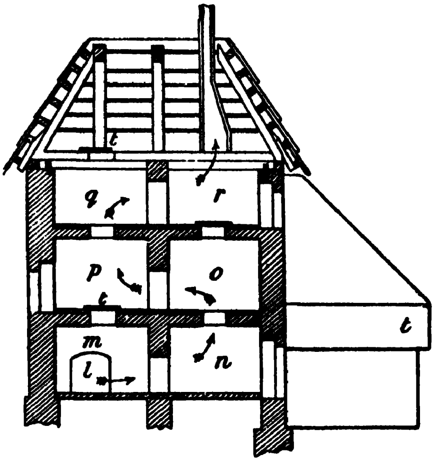


FIG. 4.—VERTICAL SECTION OF 'POISON TOWER.'

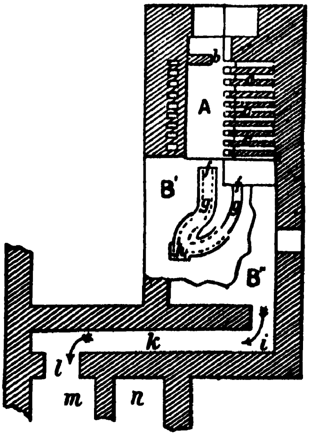
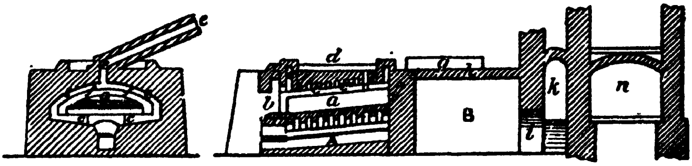


FIG. 5.—GROUND PLAN OF FURNACE.

Roasting in muffle furnaces.—This process is used at Altenberg (Figs. 4, 5, and 6) and at Reichenstein in Silesia (Figs. 7 and 8), where wood is cheap.

The ore, reduced to a moderate size and

known as *schleich*, is introduced through an opening in the top in charges of about 10 cwt. and spread 2 or 3 inches thick on the floor of the muffle. It is first heated to redness, and then more gently, with the muffle door open, to oxidise the mass thoroughly before sublimation. The operation is completed in 11 or 12 hours.



Transverse Section. Longitudinal Section.

FIG. 6.—SUBLIMING FURNACE.

Condensation of the oxide. — The vapours passing off in the roasting are carried through chambers so arranged that the gases come in contact with a very large condensing surface passing through a series of chambers before escaping into the air. At the Devon Great Consols and other large works, the chambers are made of thin brickwork covered with iron plates to assist the cooling of the gaseous oxide. The ores, before calcination, are dried over iron plates on the condensers.

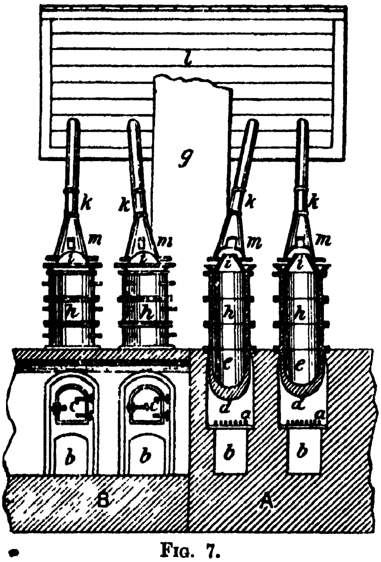


FIG. 7.

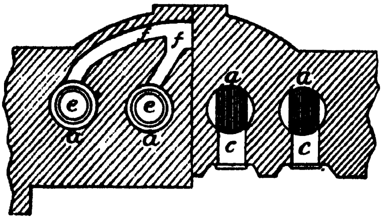


FIG. 8.—REICHENSTEIN FURNACES.

These chambers are cleared at intervals, some every fortnight, those at Silesia once in two months. Two sets of chambers are frequently used, so that one set may be working while the other is being cleared.

The oxide produced by all processes except that of the muffle is known as 'arsenical soot,' and is impure, containing carbon and sulphur compounds; when so mixed it is of a dark-grey colour and requires to be resublimed.

The condensing chambers connected with the muffles in Silesia are in a lofty building called the 'poison tower' (*Giftthürme*). The gases traverse, by a sinuous course, a series of chambers, depositing the finest product in the lower ones, that in the upper chambers containing sulphur. The chambers are cleared about every 2 months, and contain about 25 tons of white arsenic ('poison flour,' or *Giftmehl*). Being comparatively pure, it does not usually require refining, but may be at once converted into arsenical glass. The workmen engaged in clearing the chambers are clothed in leathern garments with glazed apertures for the eyes, and wear wet cloths over their mouths and noses to absorb the irritating fumes. It is stated at Salzburg that only 'arsenic-eaters' can perform this work continuously.

Refining or resublimation.—For this purpose a reverberatory furnace is used, which is usually much shorter than that in which the calcination is performed. The arsenical soot is charged from the top and paddled down through doors at the side, more being added as it sublimes. The fuel used is smokeless, usually a mixture of anthracite and coke.

The sublimate is collected in chambers similar to those already described. It is white, glistening, and minutely crystalline. It is ground between millstones, and is thence fed into kegs from a hopper through a leathern hose which fastens to the top of the cask and prevents any escape of the powder.

Arsenic glass, or vitreous white arsenic, is prepared by volatilisation of the powder under slight pressure. For this purpose, at Swansea, a cast-iron pan is used 2 feet in diameter and surmounted by a bell 2 feet 6 inches high. The pan is heated to a cherry red, and about ¼ cwt. of refined white arsenic introduced through an opening in the top of the bell, which is then closed with a plug. In about 2 hours the whole has evaporated and condensed on the bell as a transparent glass; more white arsenic is then introduced and condensed, until after 24 hours the glass has reached a thickness of about 1 inch. The later charges, owing to the condensing surface being hotter, require about twice as long to condense as the first.

At Silesia the subliming pots are deeper and of greater capacity; they are surmounted by iron drums and conical caps, which condense the 'glass' and open into condensing chambers. The temperature is carefully regulated. The arsenic glass produced amounts to about 92 p.c. of the 'flowers' used.

Analyses of Arsenic Powder and Arsenic Glass.

(1) Powder from Altenberg, from the condenser of a tin roasting furnace, near the furnace end (Lampadius).

(2) Do. from further end of condenser (Lampadius).

(3) Do. from Oberschlema (Lampadius).

(4) Arsenic glass from Andreasberg (Streng).

	(1)	(2)	(3)	(4)
Arsenious oxide .	90·1	95·85	94·31	98·2
Arsenious sulphide .	2·05	0·32	1·03	—
Bismuth . . .	—	—	0·25	—
Sulphur . . .	0·73	0·71	0·60	—
Ore-dust . .	5·51	2·05	3·05	—
Antimonious oxide .	—	—	—	1·68

Properties and uses of arsenious oxide.—White arsenic occurs in the amorphous or glassy form, and in two crystalline modifications: (1) the octahedral or common form, of sp.gr. 3·874 at 0°, and (2) in trimetric prisms, occasionally found in sublimates; this form is converted into the octahedral variety when heated or boiled in water.

The amorphous form is transparent when first prepared, but becomes opaque when exposed to the air, especially when damp, diminishing slightly in specific gravity and forming the crystalline oxide. The action commences at the outside, so that even after a considerable time a piece is frequently found with a transparent nucleus. The vitreous form may be kept in a scaled glass tube unchanged for years.

The vitreous form, according to Buchner, is soluble in 108 parts of cold water, whilst the opaque form requires 355 parts; the solubility of an ordinary piece is therefore doubtful, depending on the amount of change it has undergone. It is very soluble in glycerol, and is stated by Jackson to form *glyceryl arsenite* (Chem. News, 49, 258).

On making a strong solution of the *vitreous* form in dilute hydrochloric acid by dissolving 3 parts in a mixture of 12 hydrochloric acid and 4 water, and slowly cooling, it is deposited in the octahedral form, each crystal as it falls producing a flash of light (H. Rose). If these crystals be redissolved or if the opaque form be used, no light is produced on crystallising, that phenomenon appearing to depend on the change of the amorphous into the crystalline form at the moment of crystallisation.

At about 193° arsenious oxide softens and sublimes without fusion; it fuses under pressure; its vapour is colourless and odourless. It is acid to test papers, but does not appear to form true arsenious acid on solution in water.

Arsenious oxide is a powerful febrifuge, being sometimes efficacious when quinine has failed. It is highly poisonous, 2 or 3 grains being a very dangerous dose. When used habitually, however, comparatively large quantities may be taken with impunity. The inhabitants of Styria eat it under the name of 'hydrach,' to increase their endurance. Many authentic cases are recorded of 6 grains and upwards being taken without ill effect. Arsenic-eaters are stated to be fresh complexioned, with a tendency to stoutness, to be long-lived, but to die suddenly. The workmen engaged in the manufacture of dyes where arsenic acid is used have been observed to have this tendency to stoutness (*v.* Roscoe, Mem. of Lit. Phil. Soc. Manchester, 1860). In cases of death from poisoning, the greater part of the arsenic appears to be contained in the liver and intestines; of the bones, those of the pelvis and neighbouring vertebræ appear to contain most.

Arsenious oxide is adsorbed by ferric hydroxide under conditions which have been studied by Lockemann and Lucius (Zeitsch. physikal. Chem. 1913, 83, 735). The total adsorption follows the formula $E = \beta A^p$, in which E represents the mg. of iron hydroxide, A the number of mg. arsenic per 100 c.c., and β and p are constants, which differ for different temperatures. The total adsorption is not materially influenced by the presence of sodium or ammonium salts. The precipitation of arsenic by iron hydroxide is a usable process for the purification of concentrated salt solutions, and for the detection of small traces of arsenic in solutions or nitre fusions

In manufactures, arsenious oxide is used; in glass-making, to remove the colour produced by the lower oxides of iron; in enamelling; in calico-printing; as a constituent of white fire in pyrotechny; for the prevention of boiler incrustations (40 parts white arsenic to 9 sodium carbonate); in the manufacture of arsenic acid; and of fly and rat poisons; and in the manufacture of a large number of pigments, arsenic being found in green, blue, pink, white, brown, and other colours. As a preservative it is thrown into the holds of ships, to prevent vegetable decomposition; as a wash for walls in India, to prevent insect ravages; to prevent smut in wheat; and with sodium carbonate as a wash for sheep; and in arsenical soap, for preserving skins.

Arsenious oxide is employed in the fixation of aniline colours, especially of aniline blue. It is used principally for preparing steam colours, either as a solution in glycerol containing 4 lbs. of the oxide to 1 gallon of glycerol, under the name 'arsenic and glycerine standard'; or as sodium arsenite, dissolved in sodium carbonate or borate.

In medicine it is used as Fowler's solution, which contains 4 grains of the oxide (in the form of sodium arsenite) in each ounce of fluid. In India it has been used as a cure for hydrophobia and serpent poisoning. In veterinary surgery it is largely used as a tonic, to eradicate worms, and for improving the coats of horses.

It occurs, either as an impurity or as an adulterant, in a large number of commercial products. Besides the ordinary commercial compounds in which arsenic is expected to be present, it has been found in caustic soda, potassium chlorate, commercial glucose (Clouët and Ritter), and in wine free from artificial colouring matter (traced to sulphuric acid used in purifying the casks). Dr. Tidy found about 38 p.c. of arsenious oxide in some 'violet powder' which had caused the death of at least two children (Lancet, Aug. 21, 1878).

In the year 1900 occurred a serious epidemic of arsenic-poisoning due to contamination of beer through the use of brewing sugars, glucose, or 'invert' sugar containing arsenic. The arsenic was introduced by the use of highly arsenical sulphuric acid in the production of the sugars. The total number of persons who suffered in consequence of the epidemic was certainly 6000, and probably considerably greater. At least 70 deaths were attributed to the epidemic.

Coal or coke used for malt drying always contains arsenic; with an ordinary malt kiln part of the arsenic volatilises and may deposit on the malt. Various methods have been tried and adopted in which it has been found that access of arsenic to malt may be obviated or diminished (Royal Commission: Arsenical Poisoning, 1903).

(For a statement of the amount of arsenic in the varieties of pyrites, and of its distribution in the preparation of sulphuric acid and alkali, v. H. Smith, Phil. Mag. [4] 44, 370; Chem. News, 26, 176; and C. Hjelt, Dingl. poly. J. 226, 174–181.)

Fresenius finds that the arsenic in many chemical glasses is removed by alkaline, but not by acid liquids; the bearing of this on judicial investigations is important.

The commercial article is frequently adulterated with gypsum, chalk, &c., these may easily be detected by heating a little on a knife, when they will remain after the oxide has volatilised.

Sodium arsenite. *Acid sodium arsenite*

$$Na_2O{\cdot}2As_2O_3{\cdot}2H_2O$$

is prepared by dissolving arsenious oxide in a solution of caustic soda or sodium carbonate, and evaporating the solution. The neutral salt, $Na_2O{\cdot}As_2O_3$, is formed by boiling this compound for some time with sodium carbonate, and washing the residual salt with alcohol (Pasteur).

Potassium arsenite is prepared in a similar manner.

Sodium arsenite is used as a substitute for dung in dyeing, but is not so reliable as the arsenate. It enters into the composition of all preparations in which arsenious oxide is dissolved with sodium carbonate.

A solution undergoes slow oxidation on warming in contact with air.

An arsenite of chromium and iron is used as a green pigment in wall-papers.

Scheele's green. *Arsenite of copper. Hydrocupric arsenite.* $CuHAsO_3$.

According to Scheele's method, 11 oz. arsenious oxide are gradually added to a solution of 2 lbs. potassium carbonate in 10 lbs. boiling water; this is filtered and poured into a solution of 2 lbs. copper sulphate in 30 lbs. water, so long as a grass-green precipitate falls. The precipitate is thrown upon a filter cloth, washed with warm water, and dried gently with the production of about 1½ lbs. of the pigment.

Scheele's green is a pulverulent, fine light-green colour, formerly largely used in calico-printing and for wall-papers. It is, however, much less used at the present time. It dissolves entirely in excess of alkali or in acids.

Schweinfurth green. *Imperial green. Emerald green. Mitis green. Aceto-arsenite of copper* (when mixed with gyspum or heavy spar, known also as *Mountain* or *Neuwieder green*).

$$3CuOAs_2O_3{\cdot}Cu{\cdot}(C_2H_3O_2)_2$$

Five parts of verdigris (basic copper acetate) are made into a thin paste with water and added to a boiling solution of rather more than 4 parts arsenious oxide in 50 parts water; the solution is kept boiling during the mixture. If a yellow-green precipitate falls, a little acetic acid is added, and the solution boiled a few minutes longer; the precipitate becomes crystalline and soon acquires the characteristic green colour.

A very fine product is prepared by the following method:—Boiling, concentrated solutions of arsenious oxide and copper acetate are mixed in such proportions that equal weights of the two substances are present when a bulky olive-green precipitate falls; an equal bulk of cold water is then added and the mixture placed in a flask which it fills to the neck, thus preventing any pellicle which may form on the surface from falling through the liquid and causing a premature crystallisation. The colour under these circumstances takes two or three days to perfect, the beauty of the product being much increased by slow formation. The workmen engaged in the preparation of this pigment do not appear to be injured by it. In contact with organic matter it is, however, liable to change. By the action of damp and moulds, such as *Penicillium brevicaule, Aspergilli,* &c., on paper coloured with this pigment a peculiar odour is frequently produced, which appears to be due to the formation of diethylcacodyl oxide $[As(C_2H_5)_2]_2O$, unaccompanied, as formerly supposed, by arseniuretted hydrogen (Klason, Ber. 1914, 47, 2634).

Arsenic oxide. *Arsenic acid, Arsenic pentoxide, Acide arsénique, Arsensaure, Acidum arsenicum.* As_2O_5.

Produced when arsenious oxide is acted upon by an oxidising agent.

On the large scale 4 parts white arsenic are gradually added to 3 parts nitric acid of not less than 1·35 sp.gr. in a vat capable of holding from 65 to 70 kilos. of white arsenic. Great heat is produced and the evolved fumes are passed over coke moistened with water, whereby about two-thirds of the nitric acid is recovered. In 24 hours a syrupy liquid is formed, containing a small quantity of arsenious oxide, which may be oxidised with a little more nitric acid.

Kestner performs the oxidation in large glass flasks, the nitrous fumes being passed through lead pipes and condensed in leaden chambers.

Arsenic oxide has also been prepared by suspending arsenious oxide in water, passing a current of chlorine through the liquid, and evaporating the solution thus produced.

It is a deliquescent solid fusing at a dull-red heat, of acid metallic taste and acid reaction. It dissolves in 6 parts cold and in 2 parts hot water. The solution evaporated in an open vessel at 50°, or under increased pressure at 150°, deposits crystals of the composition $3As_2O_5{,}5H_2O$. Above 200° crystals of As_2O_5

separate. Concentrated solutions crystallising spontaneously or by freezing deposit the hydrate $H_3AsO_4\frac{1}{2}H_2O$, or mixtures of this with $3As_2O_5,5H_2O$ (Balareff, Zeitsch. anorg. Chem. 1911, 71, 73). A cold, strong solution blisters the skin. Arsenic oxide and its salts are less poisonous than the corresponding arsenious compounds.

Sodium arsenate. *Hydric disodic arsenate*; '*Dung salt.*' Na_2HAsO_4.

It is prepared by saturating arsenious oxide with crude soda ash, drying, and deflagrating with sodium nitrate in a reverberatory furnace.

Arsenate of soda is largely used in calico-printing as a substitute for dung, its feebly alkaline properties rendering it useful for that purpose.

Arsenate of iron is an amorphous green powder containing 33·6 p.c. arsenic.

Arsenic sulphides. Arsenic forms three well-defined sulphides, As_2S_2, As_2S_3, and As_2S_5, the two former occurring naturally. A large number of other sulphides of indefinite composition also exist.

Arsenic disulphide or **Realgar.** *Ruby sulphur. Rothes Rauschgelb. Rothes Schwefel. Sulphuré rouge. Orpin rouge. Risigallo. Sandaraca.* As_2S_2.

Prepared by fusing together arsenic and sulphur or orpiment in the proper proportions. On the large scale it is obtained by distilling a mixture of arsenical ores, such as arsenical and iron pyrites, with sulphur or with the sulphide of arsenic precipitated in the purification of sulphuric acid.

The mixture should contain about 15 p.c. arsenic and 26–28 p.c. sulphur; it is placed in flask-shaped earthenware retorts, holding about 60 lbs. when two-thirds full, which are connected with similar receivers. The retorts are gradually heated to redness and kept so for 8–12 hours. The crude realgar should be compact, dark, and rich in arsenic; if sulphur be in excess it is friable and light red. It is re-melted rapidly in cast-iron pans with the requisite amount of sulphur or arsenic, or with realgar of poorer quality. The mass is cleared of slag and heated until quite fluid, and until a small quantity shows the proper appearance on cooling. It is then poured into conical sheet-iron moulds.

Greater care is necessary in the preparation of realgar than of orpiment, and an assay is frequently made to ascertain the exact proportions required before the final melting.

It is hard and brittle, generally opaque, with vitreous conchoidal fracture, orange or hyacinth red in mass and orange-red in powder. Its sp.gr. is 3·4–3·6, and its usual composition is arsenic 75, sulphur 25. It volatilises easily before the blowpipe with a smell of garlic and burning sulphur, is insoluble in water or hydrochloric acid, but soluble in alkaline sulphides.

Realgar is a constituent of blue fire and of 'white Bengal fire,' which is used as a signal light, and consists of realgar 2, sulphur 7, potassium nitrate 24.

The finest variety, especially that which occurs native, is used as a pigment by artists.

Arsenic trisulphide or **Orpiment.** *Operment. Gelbes Rauschgelb. Risigallum. Auripigmentum* (of which its usual name is a corruption). *Yellow Sulphide of Arsenic.* As_2S_3.

This sulphide is formed as a yellow precipitate when sulphuretted hydrogen is passed through a solution of arsenious acid in hydrochloric acid.

Precipitated arsenious sulphide is appreciably decomposed by water, and even by alcohol, with formation of hydrogen sulphide. It is also attacked to a considerable extent by dilute hydrochloric acid, but the action of dilute acid or of water is checked by the addition of hydrogen sulphide. The precipitate is apt to contain arsenic hydrosulphide $As(SH)_3$, together with arsenious oxide (Schmidt. Arch. Pharm. 1917, 255, 45).

On the large scale it is prepared by subliming sulphur with arsenious oxide, 2 parts of arsenious oxide and 1 part sulphur being a common proportion; the colour of the product is lighter when less sulphur is used.

According to R. Wagner, a very fine colour may be produced as follows:—2 parts finely ground barium sulphate are calcined with 1 part powdered charcoal or other carbonaceous matter, and the product is pulverised, mixed with 1 part ground orpiment, boiled in water and filtered. The solution, containing a sulpharsenite of barium, is precipitated by the addition of sulphuric acid. By the addition of a suitable amount of barium chloride before precipitation, the pigment may be correspondingly lightened in colour.

Orpiment is insoluble in water but very soluble in alkaline sulphides. It was formerly much used as a pigment under the name of King's Yellow, but now is largely replaced by chrome yellow. The lighter varieties contain as much as 80 to 90 p.c. of arsenious oxide, and are consequently very poisonous. The darker varieties contain from 1 p.c. to 15 p.c. of the oxide and from 0·2 to 3 p.c. non-volatile matter. It is used in pyrotechny, and the finer kind, especially the mineral, is made into pigment for artists.

It was formerly used as a deoxidising agent in the reduction of indigo blue, and in ammoniacal solution in silk-dyeing. A mixture of 9 orpiment and 1 quicklime made into a paste with water is used under the name of 'Rusma' for removing hair from skins, but is now generally replaced by the solution of sulphide of lime prepared from the spent lime gasworks.

Schultze (J. pr. Chem. 25, 431) considers that another form of the trisulphide exists which is soluble in water (*v.* COLLOIDS). For a description of its properties, *see* Dumanski, Zeitsch. Chem. Ind. Kolloide, 1911, 9, 262.

Arsenic pentasulphide As_2S_5. Berzelius in 1826 stated that this compound was formed when sulphuretted hydrogen is passed through a moderately concentrated solution of arsenic acid, but the precipitate was generally considered to be a mixture of the trisulphide and sulphur. Bunsen in 1878 showed that it was produced on passing a rapid current of sulphuretted hydrogen through a hot hydrochloric acid solution of an alkaline arsenate, and his results were confirmed by McCay in 1887 (*cf.* Brauner and Tomíček, Chem. Soc. Trans. 1888, 147; Travers and Usher, Chem. Soc. Trans. 1905, 87, 1370; and Foster, J. Amer. Chem. Soc. 1916, 38, 52).

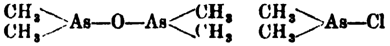
Arsenic pentasulphide is totally insoluble in water, alcohol, or disulphide of carbon. The dry substance, on rubbing in a mortar, becomes strongly electrical.

Arsenic chloride. *Butter of arsenic. Caustic oil of arsenic* $AsCl_3$ is produced by the action of chlorine on arsenic; by distilling arsenic with mercuric chloride; by heating dry arsenious oxide with sulphur monochloride at 100°–125°: $As_4O_6+6S_2Cl_2=4AsCl_3+3SO_2+9S$, and by distilling arsenious oxide with strong hydrochloric acid. It is a colourless, oily liquid, of sp.gr 2·205 0°/4° boiling at 130·2° (Thorpe). A solution of arsenious oxide in strong hydrochloric acid loses arsenic on evaporation, but unless concentrated the loss by volatilisation is small. A *N*/10 solution of arsenious chloride, *N*/1 as regards acidity, may be concentrated to half-bulk without loss of more than one-thousandth part of the arsenic present.

Arsenic tri-iodide forms garnet to scarlet red hexagonal crystals: obtained by mixing arsenious oxide with iodine, and, after standing, extracting with carbon disulphide.

The chloride and iodide are used to a slight extent in medicine. H. W. H.

ARSENICALS, ORGANIC. HISTORICAL. The study of organo-arsenical compounds dates from the discovery of 'Cadet's fuming arsenical liquid,' a compound with an intolerable stench, and the singular property of spontaneous inflammability in air at ordinary temperatures to which L. C. Cadet de Gassicourt refers in his memoir on the production of sympathetic inks published in 1760. This liquid formed the distillate when equal parts of arsenious oxide and potassium acetate were heated in a glass retort. Guyton de Morveau, Morel, and Durande, who worked in Dijon, confirmed this discovery about eighteen years later, and in 1804 Thénard published further researches on the liquid (Ann. Chim. Phys. 30 Vendémiaire An. xiii. 1804, 52, 54), coming to the conclusion that the product was a complex acetate containing arsenic. The next important contribution to the subject was made in 1837 (Pogg. Ann. 1837, 40, 219; 42, 145; *v.* Annalen, 1837, 24, 27; 1839, 31, 175) when Robert Wilhelm Bunsen commenced his classical researches, which were carried on for a period of six years. He showed that the distillation product of arsenious oxide and potassium acetate contained the oxide of an arseniuretted radical, a group containing arsenic, carbon, and hydrogen which remained unchanged in composition when the oxygen was replaced by the halogens, sulphur or cyanogen. At first Bunsen supposed that the product contained no oxygen, and was C_2H_6As, and as this formula represents alcohol in which oxygen is replaced by arsenic, he adopted the name *Alkarsin* for the supposed arsenical analogue of alcohol. Berzelius suggested the presence of oxygen in Bunsen's 'Alkarsin' (*i.e.* the original distillate), and gave the name *Kakodyl* (Gr. kákos-odyl) to the compound radical which functioned as a 'compound element' in the series of reactions of 'alkarsin.' It is now evident that the distillate dealt with by the early workers must have contained, according to experimental conditions, varying amounts of cacodyl oxide and cacodyl, and this would account for the lack of uniformity in the interpretation of the results and for some temporary confusion in nomenclature. Further systematic investigation by Bunsen (Annalen, 1841, 37, 1–57; 1842, 42, 14–46; 1843, 46, 1–48) showed that the main constituent of Cadet's liquid is cacodyl oxide, which he was able to prepare in a pure state ('paracacodyl') by the hydrolysis of cacodyl chloride with potassium hydroxide. He also oxidised cacodyl oxide further to cacodylic acid (alkargen), and finally he isolated the radical cacodyl itself. The inner structure of the cacodyl radical was not investigated by Bunsen, but Frankland, Kolbé, and others have since shown that the radical may be regarded as tervalent arsenic associated with two methyl radicals. The cacodyl radical is $As(CH_3)_2$, and in the free state this univalent complex doubles on itself to give cacodyl $As_2(CH_3)_4$. Cacodyl oxide and cacodyl chloride have the structures:



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!As{-}O{-}As\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}\qquad\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!As{-}Cl$$

Arsenical compounds containing aromatic radicals were first investigated by Béchamp (Compt. rend. 1860, 50, 872; 51, 356; 1863, 55, 1172), who, studying the oxidising action of arsenic acid on aniline (*cf.* MAGENTA), noted that a colourless condensation product could be obtained. This substance functioned as a monobasic acid, and Béchamp assumed that the compound was an anilide of ortho- arsenic acid $C_6H_5{\cdot}NH\ AsO(OH)_2$.

Ehrlich and Bertheim have since shown (Ber. 1907, 40, 3292) that the product is *p*-aminophenylarsinic acid $NH_2{\cdot}C_6H_4{\cdot}AsO(OH)_2$. The sodium salt

$$NH_2{\cdot}C_6H_4{\cdot}AsO(OH){\cdot}ONa,xH_2O$$

(x=2–6 in various preparations) is the *Atoxyl* of therapeutics.

Ehrlich, who observed that aromatic compounds containing tervalent arsenic as distinct from the quinquevalent Atoxyl series had a more pronounced action in protozoal diseases, now instituted very extensive researches which, after 605 trials, culminated in the preparation of *Salvarsan*, or '606,' in 1910. *Neosalvarsan*, or '914,' was discovered in 1911, and both these substances have been highly successful in the arsenical treatment of syphilis.

More recent work has trended in the direction of increasing in these substances the trypanocidal power and reducing toxicity to the patient. Co-ordination compounds of salvarsan with heavy and noble metals have been investigated. *Luargol*, which has met with great success in the French Army, is a complex of salvarsan, silver bromide, and antimony. The preparation of primary arsines by Palmer and Dehn (Ber. 1901, 34, 3594) has prompted further researches on organo-arsenic compounds of therapeutic value. The discovery that the diazo- reaction could be applied to the synthesis of aromatic arsenicals has given a further impetus to the study of these compounds (Bart, D. R. P. 250264; Eng. Pat. 568, 1911).

CACODYL AND ITS MORE IMPORTANT DERIVATIVES (Bunsen, Annalen, 1842, 42, 14).

Cacodyl $[As(CH_3)_2]_2$, ***Tetramethyldiarsine***, a colourless, highly refractive liquid with intolerable smell; b.p. 170°; solidifies at −6°, forming square plates; vapour density 7·1; sparingly soluble in water, is prepared by treating cacodyl chloride with metallic zinc in an atmosphere of carbon dioxide. It inflames spontaneously in air, giving carbon dioxide, water, and arsenious oxide. It behaves as a univalent or tervalent radical combining with sulphur and the halogens.

Ethylcacodyl (*Tetraethyldiarsine*) $[As(C_2H_5)_2]_2$ an oil, b.p. 185°–190°, is produced, together with *triethylarsine* $As(C_2H_5)_3$, b.p. 140°, by the interaction of ethyl iodide and sodium arsenide; it yields, on oxidation, diethylarsinic acid, a soluble crystalline product (Landolt, Annalen, 1854, 89, 316; 92, 365). *Dimethyldiisoamylcacodyl* $(CH_3)_2As{\cdot}As(C_5H_{11})_2$, obtained by the following general method (Dehn, Amer. Chem. J. 1908, 40, 123):

$$R_2AsH+ClAsR'_2=HCl+R_2As{\cdot}AsR'_2$$

from a secondary arsine and a secondary arsenious chloride.

Cacodyl oxide $[As(CH_3)_2]_2O$, the main constituent of Cadet's liquid, is a heavy oil; sp.gr. 1·462/15°; b.p. 120°; solidifies at −25°; vapour density 7·55; sparingly soluble in water. It is prepared by distilling cacodyl chloride with aqueous potassium hydroxide, drying and redistilling in atmosphere of carbon dioxide (Baeyer, Annalen, 1858, 107, 282).

Cacodyl chloride $As(CH_3)_2Cl$, colourless liquid, heavier than water; b.p. 100°; vapour density 4·56; is insoluble in water. It has a penetrating, stupefying odour, and has a marked irritating action on the mucous membrane of the nose.

Concentrated hydrochloric acid and mercuric chloride are added successively to Cadet's arsenical liquid, and the resulting crystalline magma is liquefied by the addition of more hydrochloric acid and distilled. The distillate containing cacodyl chloride is purified by treatment with calcium carbonate to remove the acid, and with anhydrous calcium chloride to remove water.

Cacodyl cyanide $As(CH_3)_2CN$, colourless prisms; m.p. 33°; b.p. 140°; sublimes readily at ordinary temperatures to an exceedingly poisonous vapour. Is soluble in alcohol and ether, sparingly soluble in water. It is prepared by interaction between cacodyl and mercuric cyanide:

$$[As(CH_3)_2]_2+Hg(CN)_2=Hg+2As(CH_3)_2CN$$

Cacodyl sulphide $[As(CH_3)_2]_2S$, colourless oil; b.p. well above 100°; insoluble in water; miscible with ether and alcohol.

Cacodyl disulphide $[As(CH_3)_2]_2S_2$, white rhombic plates; m.p. 50°. *Cacodyl cuprisulphide* $Kd_2S,3Cu_2S$, lustrous octahedra.

Cacodylic acid. Dimethylarsinic acid.

$$As(CH_3)_2O{\cdot}OH,$$

(Bunsen, Annalen, 1843, 46, 2), inodorous colourless prisms; m.p. 200°; very soluble in water and alcohol. Is prepared by the oxidation of cacodyl oxide with mercuric oxide under water. It is very stable, not decomposed by the strongest oxidising agents; it forms crystallisable salts, certain of which have been used in medicine, including sodium cacodylate $KdO_2Na,3H_2O$ (Ph. Helv.).

Cacodyl trichloride $(CH_3)_2AsCl_3$ (Baeyer, Annalen, 1858, 107, 263), which crystallises from ether in prisms or leaflets, is very unstable, fumes in air, and decomposes at 40°–50° into *methylarsenious chloride* $CH_3{\cdot}AsCl_2$ and methyl chloride.

SYNTHESES OF ALIPHATIC ARSENICALS.

I. Interaction of an Alkyl Halide with an Alloy of Arsenic (Cahours, Compt. rend. 1859, 49, 87).

Methyl iodide reacts at 180° with zinc or cadmium alloys of arsenic, yielding double salts of the formulæ:

$$2As(CH_3)_4I,ZnI_2 \text{ and } 2As(CH_3)_4I,CdI_2$$

From these, tetramethylarsonium iodide is obtained by treatment with caustic alkali.

II. Interaction of an Alkyl Halide with Elemental Arsenic.

A modification of the first method by which the alkyl halide and arsenic are heated together in a sealed tube at 160°–200° (Cahours, Annalen, 1862, 122, 200). If amorphous arsenic be used the reaction may be brought about at ordinary temperatures (Martindale, Congress of Applied Chemistry, 1909). In either case a double salt, *e.g.* $As(CH_3)_4I,AsI_3$ is formed, and this, when decomposed by caustic potash, gives potassium arsenite, potassium iodide, and tetramethylarsonium iodide

III. Interaction of a Metallic Alkyl with an Arsenic Halide.

Zinc dimethyl reacts with arsenious chloride giving *trimethylarsine* (Hofmann, Jahresber. 1855, 538; Annalen, 1857, 103, 357).

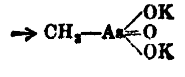
Mixed arsines may be prepared in this way: *e.g.* dimethylarsenious chloride reacts with zinc diethyl giving *dimethylethylarsine.*

The Grignard reaction—a special case of this method—affords an important means of preparation of organo-arsenic compounds (Hibbert, Ber. 1906, 39, 160). Arsenious bromide treated with excess of Grignard reagent (magnesium methyl iodide) yields *trimethylarsine.*

IV. Alkylation of Arsenical Oxy- Compounds.

In this process, due in the first place to G. Meyer (Ber. 1883, 16, 1440), but since generalised by Klinger and Kreutz (Annalen, 1888, 249, 147), and by Dehn and McGrath (Amer. Chem. J. 1905, 33, 138; 1906, 28, 351), sodium arsenite is treated with alkyl iodide in alkaline solution giving sodium alkylarsenate.

This synthesis, unlike the preceding methods, which require anhydrous solvents or an inert atmosphere, can be carried out in aqueous solutions under ordinary atmospheric conditions. Potassium methylarsinate is produced by mixing together potassium arsenite and methyl iodide in aqueous methyl alcoholic solution. After several days a white precipitate $2As_2O_3,KI$ is removed and potassium methylarsinate is obtained from the filtrate:



Dealkylation of Aliphatic Arsenicals.

This process, originally due to Baeyer (Annalen, 1858, 107, 282), who confirmed and extended Bunsen's work, is effected by converting cacodyl chloride into cacodyl trichloride by direct addition of chlorine and by distilling the trichloride, when methyl chloride is eliminated, and methylarsenious chloride CH_3AsCl_2 is produced. This monoalkylated arsenical is successively chlorinated and hydrolysed; the final product, methylarsinic acid, is a substance of therapeutic utility, having been employed in the form of its sodium salt $CH_3{\cdot}AsO(ONa)_2,H_2O$, arrhenal or new cacodyl (Auger, Compt. rend. 1903, 137, 925; Auger and Billy, *ibid.* 1904, 139, 599).

ALIPHATIC ARSENICALS.

Trimethylarsine $As(CH_3)_3$, liquid; b.p. 70°; synthesised by method III. (above). Is also prepared by distilling tetramethylarsonium iodide $As(CH_3)_4I$ with dry potassium hydroxide. Tetramethylarsonium iodide is a solid crystallising in colourless leaflets, which decompose at 170°-180°. It is synthesised by method II. (above).

Tetramethylarsonium hydroxide, obtained by the action of moist silver oxide on the iodide, is a strongly caustic soluble substance resembling sodium or potassium hydroxide.

Methylarsinic acid $CH_3{\cdot}AsO(OH)_2$, anhydrous colourless crystalline solid; m.p. 161°; soluble in water and alcohol; decomposes carbonates and forms an ammonium salt. The sodium salt, arrhenal or new cacodyl $CH_3{\cdot}AsO(ONa)_2H_2O$, has been used in medicine, as also have sodium dimethylarsinate (sodium cocodylate)

$$(CH_3)_2AsO_2Na,3H_2O$$

and corresponding salts of magnesium, iron, strychnine, guaiacol, and antipyrine.

Dimethylarsine $(CH_3)_2AsH$, colourless liquid with odour of cacodyl; b.p. 35·6°; spontaneously inflammable in air above 10° (Palmer, Ber. 1894, 27, 1378; Dehn and Wilcox, Amer. Chem. J. 1906, 35, 3).

Strong hydrochloric acid is dropped slowly on to a mixture containing crude cacodyl oxide, amalgamated zinc-dust and alcohol. The distillate is passed through a water wash-bottle and a soda lime tube to a condenser surrounded by a freezing mixture of ice and salt.

Methylarsine $CH_3{\cdot}AsH_2$ (Palmer and Dehn, Ber. 1901, 34, 3594), volatile, colourless, highly refractive liquid with odour of cacodyl; b.p. 2°; very poisonous, not spontaneously inflammable; practically insoluble in water; soluble in alcohol, ether, or carbon disulphide; is prepared by reducing methylarsinic acid with amalgamated zinc-dust and alcoholic hydrochloric acid with precautions similar to those taken in the preparation of dimethylarsine.

Arsenomethane $(CH_3{\cdot}As:As{\cdot}CH_3)_2$ (Auger, Compt. rend. 1904, 138, 1705), heavy yellow oil with garlic odour; b.p. 190°/13 mm. Is prepared by reducing sodium methylarsinate with sodium hypophosphite and sulphuric acid.

VOLATILE ARSENICAL COMPOUNDS FROM MOULDS.

It has been observed that wallpapers and carpets containing arsenical pigments have become a source of danger owing to the evolution of volatile arsenic compounds of a decidedly poisonous character. It is now known that the presence of certain moulds is a necessary condition for the production of such gases. These moulds, the most important of which is *Penicillium brevicaule*, evolve a volatile arsenic compound when cultivated in a medium containing sodium arsenite. Several observers have examined this phenomenon, and P. Biginelli has prepared fairly well-defined solid derivatives of the gas and thereby concludes that the gas itself is *diethylarsine* $(C_2H_5)_2AsH$ (Atti. R. Accad. Lincei, 1900 [v.] 9, ii. 210, 242), although his results have not yet been confirmed by the isolation of the secondary arsine itself.

SYNTHESES OF AROMATIC ARSENICALS.

Two general methods are due to Michaelis, who, in collaboration with many pupils, has given them a very wide application (Ber. 1876, 9, 1566; Annalen, 1880, 201, 184).

I. Interaction of the Arsenic Halide with a Diaryl Derivative of Mercury.

The mercury diaryl derivative is prepared by the action of sodium amalgam on the aryl bromide. The action of the mercury diaryl takes place in two stages. In the first, the *arylarsenic dihalide* is produced, *e.g.*

$$Hg(C_6H_5)_2+2AsCl_3=HgCl_2+2C_6H_5{\cdot}AsCl_2$$

If the action is carried further the diaryl arsenic halide is formed

$$Hg(C_6H_5)_2+2C_6H_5{\cdot}AsCl_2=2(C_6H_5)_2AsCl+HgCl_2$$

A modification of this method has been employed (Ber. 1914, 47, 2748), whereby the arylmercuric chloride is heated at 100° with arsenious chloride with the production of the arylarsenious chloride.

II. Interaction of Sodium with Chloroaryls and Arsenious Chloride (or the corresponding bromo- derivative).

This process is a modification of Fittig's synthesis of hydrocarbons, *e.g.*:

$$AsCl_3+3C_6H_5{\cdot}Cl+6Na=6NaCl+As(C_6H_5)_3$$

The tertiary arsine thus formed readily forms dihalides which on heating give secondary arsenic halides:

$$(C_6H_5)_3AsCl_2=C_6H_5{\cdot}Cl+(C_6H_5)_2AsCl$$

Primary derivatives can be formed by heating the tertiary arsine with arsenious chloride under pressure at 250°; the secondary compound is formed at the same time:

$$(C_6H_5)_3As+2AsCl_3=3C_6H_5AsCl_2$$
$$2(C_6H_5)_3As+AsCl_3=3(C_6H_5)_2AsCl \text{ (by-product)}$$

III. Grignard Reaction.

To the foregoing processes due to Michaelis this reaction adds a third method which has been applied with considerable success to the synthesis of triphenylarsine and its homologues.

IV. Diazo- Synthesis.

Aromatic primary amines are converted into the corresponding arylarsinic acids by treating the diazonium salt or alkali diazooxide with aqueous sodium arsenite with or without copper powder (Bart, D. R. PP. 250264; 254345).

AROMATIC ARSENICALS.

Phenylarsenious chloride $C_6H_5\cdot AsCl_2$ (La Coste and Michaelis, Ber. 1878, 11, 1883), colourless, highly refractive viscous liquid; b.p. 252°–254°; with pungent odour, more pronounced on warming; very irritating action on the skin.

Arsenobenzene $C_6H_5\cdot As:As\cdot C_6H_5$ (Michaelis and Schulte, Ber. 1881, 14, 912; 1882, 15, 1952), light yellow needles; m.p. 196°; insoluble in water or ether; sparingly soluble in alcohol; soluble in benzene, chloroform, or carbon disulphide. An alcoholic solution of phenylarsenious oxide is warmed with excess of crystallised phosphorous acid. The pasty product yields well-defined crystals from boiling xylene.

Phenylarsinic chloride $C_6H_5\cdot AsCl_4$ (Michaelis, Ber. 1877, 10, 622), flattened yellow needles, m.p. 45°; decomposes violently in water, dissociates on warming into the dichloride and free chlorine, the action being facilitated when conducted in a stream of dry carbon dioxide. At 150° it is decomposed completely into chlorobenzene and arsenious chloride.

Phenylarsinic acid $C_6H_5\cdot AsO(OH)_2$ (La Coste and Michaelis, Annalen, 1880, 201, 184; Michaelis, Ber. 1877, 10, 626), colourless prisms passing into the anhydride at 158°, soluble in absolute alcohol; very stable towards oxidising agents; on reduction gives phenylarsine (*q.v.*).

Diphenylarsenious chloride $(C_6H_5)_2AsCl$ (La Coste and Michaelis, Ber. 1878, 11, 1885; Annalen, 1880, 201, 215), well-defined colourless tabular crystals; m.p. 38°–41° (formerly described as a yellow oil). Slight odour, more pronounced on warming. Vapour very irritating to the skin. Alkalis hydrolyse it to *diphenylarsenious oxide*, crystalline aggregates; m.p. 91°–92°, and this product reduced with phosphorous acid furnishes *phenylcacodyl* $(C_6H_5)_2As\cdot As(C_6H_5)_2$ crystalline mass; m.p. 135°.

Diphenylarsinic acid $(C_6H_5)_2AsO\cdot OH$, colourless needles; m.p. 174°. Sparingly soluble in cold water, ether, or benzene, more soluble in hot water or alcohol.

Triphenylarsine $(C_6H_5)_3As$ (La Coste and Michaelis, *l.c.*), colourless plates from alcohol; m.p. 58°–60°; b.p. above 360° (without decomposition in carbon dioxide). Very soluble in ether or benzene, sparingly soluble in alcohol.

Triphenylmethylarsonium iodide

$$(C_6H_5)_3As(CH_3)\cdot I$$

pale yellow leaflets from alcohol; m.p. 176°. Soluble in alcohol or ether, sparingly soluble in water.

Tribenzylarsine $As(CH_2\cdot C_6H_5)_3$ (Michaelis and Paetow, Annalen, 1886, 233, 60; Paetow, Inaug. Dissert. Rostock, 1885), colourless monoclinic prisms from alcohol; m.p. 104°. Insoluble in water, sparingly soluble in alcohol; soluble in ether, benzene, and glacial acetic acid. Oxidised by hot dilute nitric acid to arsenic and benzoic acids. Obtained, together with its dichloride and dibenzylarsinetrichloride, by the action of sodium on arsenious chloride and benzyl chloride.

Dibenzylarsinic acid $(C_6H_5\cdot CH_2)_2AsO\cdot OH$ (*ibid.*), leaflets from alcohol; m.p. 210°, decomposing at higher temperatures; sparingly soluble in ether, acetone, or benzene; bitter salt taste and very irritating effect on the mucous membrane.

Benzylarsinic acid $C_6H_5\cdot CH_2\cdot AsO(OH)_2$ (*ibid.*); Dehn and McGrath, J. Amer. Chem. Soc. 1906, 28, 354), colourless needles; m.p. 167°.

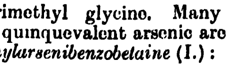
Benzylarsine $C_6H_5\cdot CH_2\cdot AsH_2$ (Dehn, Amer. Chem. J. 1908, 40, 113), light yellow liquid; b.p. 140°/260 mm.

p-*Benzarsinic acid* $CO_2H\cdot C_6H_4\cdot AsO(OH)_2$ (Michaelis, Annalen, 1902, 320, 303; Ber. 1915, 48, 870; Sieburg, Arch. Pharm. 1916, 254, 224; Bertheim, Ber. 1908, 41, 1854). This is a typical example of the carboxylated derivatives which can be obtained by oxidising arylarsinic acids containing methyl groups. This acid forms colourless plates, sparingly soluble in water, very sparingly so in alcohol and glacial acetic acid.

1. *p*-Tolylarsinic acid $(CH_3\cdot C_6H_4\cdot AsO(OH)_2)$ is treated with alkaline potassium permanganate in aqueous solution, the mixture being left for some days, when the filtrate is evaporated to dryness after acidifying with acetic acid; the residue, extracted with alcohol to remove potassium acetate, is then decomposed by concentrated hydrochloric acid when *p*-benzarsinic acid is deposited in well-defined crystals.
2. Oxidation of *p*-tolylarsinic acid by means of nitric acid in sealed tube at 170° for three hours gives a good yield of *p*-benzarsinic acid.
3. *p*-Arsanilic acid is diazotised in the presence of cuprous cyanide, the resulting *p*-cyanophenylarsinic acid, being hydrolysed by concentrated potassium hydroxide, furnishes *p*-benzarsinic acid. Its isomerides are similarly prepared.

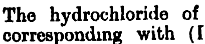
BETAINES OF AROMATIC ARSENICALS (Michaelis, Annalen, 1902, 320, 297; *ibid.* 1902, 321, 174).

Ordinary naturally occurring betaine has the constitutional formula:

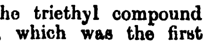


and is trimethyl glycine. Many analogues containing quinquevalent arsenic are known.

Trimethylarsenibenzobetaine (I.):



I.



II

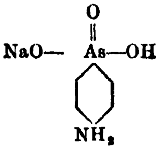
The hydrochloride of the triethyl compound corresponding with (I.), which was the first arsenical betaine to be prepared, is obtained by oxidising *p*-tolyltrimethylarsonium chloride with alkaline permanganate.

Triphenylarsenibetaine (II.). The betaine of the second type is produced by successively treating triphenylarsine with chloroacetic acid and alcoholic potash. Both these preparations have been generalised.

THE USE OF ORGANIC COMPOUNDS OF ARSENIC IN THERAPEUTICS.

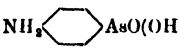
Diseases of protozoal origin, such as 'sleeping sickness,' syphilis, &c., do not, in general, lend themselves to serum treatment, and certain antiseptics which are inimicable to the existence of the protozoal parasite are quite as injurious to the tissues of the more highly organised 'host.' Nevertheless, the protozoa are more sensitive to chemical treatment than are bacteria, which are much more highly resistant, and it has been shown that it is possible to treat certain protozoal diseases with antiseptics which react specifically with the protozoa, and are yet comparatively innocuous to the host. The treatment of malaria with quinine is a typical instance of this method. With a view to their use in this branch of therapeutics, organic derivatives of arsenic, as against inorganic preparations, have been extensively investigated, and the success which has attended their use seems to be due in part to their relatively low toxicity to the higher organism, their higher solubility, which probably increases their penetration, and their comparative stability, whereby only the small fractions needful for the destruction of the protozoa become decomposed in the body, the remainder passing through the body unchanged.

Atoxyl, Sodium-p-*arsanilate*, Syn. *Arsamin, Soamin, Natrium arsanilicum.*



This salt crystallises with 2–6 molecules of water, according to the solvent used in its preparation. The corresponding mercury salt, *Asyphil*, has been used for injections.

4-Aminophenyl-1-arsinic acid (p-*Arsanilic acid*)

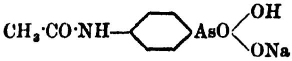


A mixture of aniline (180 grams) and arsenic acid (140 grams) is heated gradually to 170°–200° in a vessel fitted with an efficient stirrer, the temperature being maintained at 190°–200° for one to two hours. The product rendered alkaline is distilled in steam to remove excess of aniline, filtered, and neutralised with hydrochloric acid when crude *p*-arsanilic acid separates on cooling. The product dissolved in aqueous caustic soda is decolourised with animal charcoal and filtered into alcohol when sodium *p*-arsanilate (atoxyl) crystallises. A by-product, *sodium 4 : 4′-diamino diphenylarsinate* remains dissolved in the alcohol (O. and K. Adler, Ber. 1908, 41, 932; Benda and Kahn, *ibid.* 1674, 2370; Pyman and Reynolds, Chem. Soc. Trans. 1908, 93, 1184).

The foregoing condensation, due originally to Béchamp (*l.c.*), has more recently been generalised and extended to the case of the homologues of aniline containing a free para-position with respect to the amino- group (D. R. P. 219210; Eng. Pat. 14937, 1908; U.S. Pat. 913940, 1909; Welcome and Pyman, Eng. Pat. 855, 1908; Adler, Ber. 1908, 41, 931; Benda and Kahn, *ibid.* 1672). Aromatic primary amines substituted in the para-position are also amenable to the Béchamp reaction, but with the exception of *p*-nitroaniline the yields of orthoamino arsinic acids are small (Benda, Ber. 1909, 42, 3621; 1911, 44, 3294; D. R. P. 243693; Eng. Pat. 29196, 1911).

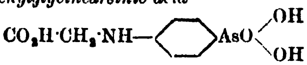
Phenol and its homologues containing free para- positions with respect to the hydroxyl group also undergo the Béchamp condensation with arsenic acid with the formation of *p*-hydroxyarsinic acids (D. R. P. 205616).

Ehrlich and Bertheim's demonstration that atoxyl was the sodium salt of *p*-amino-phenylarsinic acid rather than the anilide of arsenic acid, and that therefore atoxyl was a true organic arsenical, suggested numerous significant possibilities of syntheses, many of which have since been realised, the aim in general being directed to improvements in stability and specific action. For instance, the amino-group may be acetylated, benzoylated, or replaced by halogen or hydroxyl, or a substituted amine can be used in the initial stage of the synthesis instead of aniline. As an example of this procedure may be cited the acetylation of atoxyl, whereby a derivative is obtained which, while just as toxic to trypanosomes, is more stable and much less toxic to the host than atoxyl. This derivative:



is known as *arsacetin*, or acetylatoxyl (contains 3–4 H_2O). Large numbers of similar derivatives have been prepared, some of which have assumed commercial importance. *Benzenesulphonylatoxyl*, termed *Hectine*, has been employed in therapeutics.

Phenylglycinearsinic acid



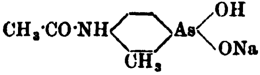
and its homologues are less toxic than atoxyl, the glycine group, which resists hydrolysis in the organism, being much more firmly attached than the acetyl group.

Atoxyl is digested with aqueous chloracetic acid in a reflux apparatus for 6–8 hours, the crystalline glycine derivative being freed from unchanged arsanilic acid by washing with dilute hydrochloric acid.

Other aromatic primary amines yield derivatives analogous to those obtained from aniline.

Sodium 2-aminotolyl-5-arsinate, '*Kharsin*,' obtained by extending the Béchamp reaction to *o*-toluidine, crystallises with 3½–5 H_2O.

Sodium acetyl-2-aminotolyl-5-arsinate '*Orsudan*' (Wellcome and Pyman, Eng. Pat. 855, 1908):



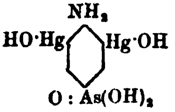
5 or 7 H_2O

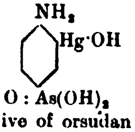
produced by acetylating the preceding compound, has also been used in protozoal diseases.

The fact that the treatment of certain protozoal diseases with azo- dyes has met with considerable success has led to the attempt to prepare dyes from the diazotisable *p*-arsanilic acid, and a number of monoazo- and polyazo-dyes have been prepared, which in the main are less toxic to the host than atoxyl and more so to protozoa.

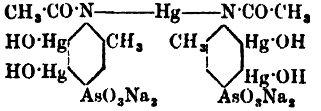
The promising results arising from the joint arsenical and mercurial treatment of syphilis suggested attempts to combine the beneficial effects in one drug, and several derivatives have been prepared which possess the anticipated properties to a more or less degree.

3 : 5-Dihydroxymercuri - 4 - aminophenylarsinic acid and 3-hydroxymercuri-4-aminophenyl arsinic acid are two well-defined examples

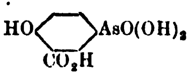




The hydroxymercuric derivative of orsudan known as '*Hydryl*,' has also given promising physiological tests :—



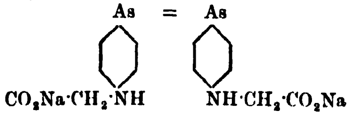
Enesol is the mercury derivative of salicyl-4-arsinic acid :



and has been employed successfully in the treatment of syphilis.

Tervalent arsenic derivatives are therapeutically of greater value than the corresponding quinquevalent derivatives, from which they are obtained by reduction.

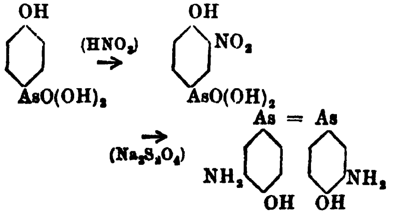
Phenylglycinearsinic acid (*q.v.*) yields *arsenophenylglycine* in reduction with sodium hydrosulphite. Its *sodium* salt, under the name *Spirarsyl* (No. 418 in Ehrlich's series) :



has been used, and is a decided improvement on atoxyl, having less toxicity for the host and greater trypanocidal power.

Similarly *p*-hydroxyphenylarsinic acid yields *p*-arsenophenol on reduction, and the fact that these substances had been used with good results in trypanosomiasis in mice led Ehrlich to prepare and examine many substances of similar constitution.

Salvarsan (Syn. *Kharsivan, Arsenobenzol, Arsenobillon, Ehrlich* 606). 3 : 3-′*Diamino*-4 : 4′ *dihydroxyarsenobenzene*, *p*-hydroxyphenylarsinic acid is successively nitrated and reduced with alkaline sodium hydrosulphite and magnesium chloride, two molecules of the compound uniting in the reduction, according to the following equation :



The foregoing *p*-hydroxyphenylarsinic acid is obtained either from *p*-arsanilic acid through the diazo- reaction, by boiling the diazo- compound with water, or directly from arsenic acid and phenol, by extending the Béchamp reaction to the latter compound.

Salvarsan can also be prepared by starting from dimethylaniline. This base, treated with arsenious chloride, yields p-*dimethylaminophenylarseniousdichloride*, oxidation of the chloride leads to p-*dimethylanilinearsinic acid*, which, on nitration, gives 3-*nitro*-4-*dimethylaminophenylarsinic acid*. The nitro- compound, on warming with 40 p.c. aqueous caustic soda, gives rise to 3-nitro-4-hydroxyphenylarsinic acid, which is reduced as above. This nitro-hydroxy compound is also obtainable by putting *p*-chloroaniline through the Bart process and successively nitrating and hydrolysing the resulting *p*-chlorophenylarsinic acid.

The crude moist preparation of salvarsan base is dissolved in methyl alcohol, and its dihydrochloride precipitated by the successive addition of methyl alcoholic hydrochloric acid and ether, and is dried in an inert atmosphere. The free base is insoluble in water or in physiological salt solution, and it does not form neutral salts, since it is an amphoteric substance, being feebly basic and having also phenolic properties.

These characteristics constitute a drawback to its utility for intravenous injections and in practice the hydrochloride has to be very carefully neutralised immediately before use by means of sodium hydroxide.

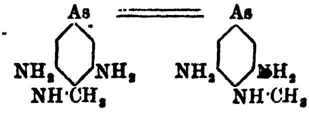
There are nine possible symmetrically constituted isomerides of salvarsan, and the following five have been obtained :—

4 : 4′	-diamino-	3 : 3′	dihydroxyarsenobenzene
2 : 2′	„	3 : 3′	„
2 : 2′	„	5 : 5′	„
4 : 4′	„	2 : 2′	„
5 : 5′	„	2 : 2′	„

In no case is the isomeride comparable in therapeutic value with salvarsan. The methylation of salvarsan increases the toxicity of the compound to the host and diminishes the trypanocidal value, *e.g.* the hexamethyl derivative is 3–5 times as toxic as the unmethylated compound, and is inactive with regard to the protozoa. Carboxylation leads to similar tendencies. Many other salvarsan derivatives have been prepared and examined.

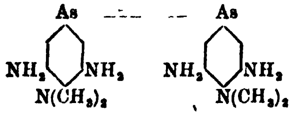
Certain polyaminoarsenobenzenes are already of considerable therapeutic importance, and significant developments in this direction seem likely. Among these salvarsan analogues the following are noteworthy :—

4 : 4′ *Dimethyl*-3 : 4 : 5 : 3′ : 4′ : 5′-*hexaminoarsenobenzene*



has low toxicity towards human beings and high trypanocidal powers.

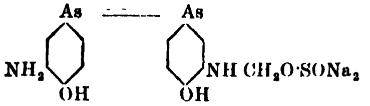
4 : 4′-*Tetramethyl*-3 : 4 : 5 : 3′ : 4′ : 5′-*hexaminoarsenobenzene*



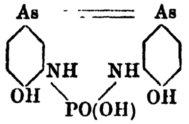
and the corresponding ethyl derivative have similar properties. These bases have the remarkable property of dissolving in soluble bicarbonates, giving rise to stable complex carbamates precipitated from aqueous solution by alcohol or acetone.

Certain limitations in the usefulness of salvarsan have already been mentioned. The drug (dihydrochloride) does not give rise to neutral solutions, and accordingly its application is lacking in simplicity. The replacement of an atom of hydrogen in one of the amino-groups of salvarsan by a methylenesulphinic group confers sufficient acidity on the molecule to enable soluble neutral and stable alkali salts to be prepared. The introduction of the methylenesulphinic group into the hydrochloride of salvarsan is brought about by the action of sodium formaldehydesulphoxylate followed successively by sodium carbonate solution and hydrochloric acid.

Sodium-3 : *3′-diamino*-4 : *4′-dihydroxyarsenobenzene*-N-*methylenesulphinate, Neo-salvarsan* is the sodium salt of the acid thus produced



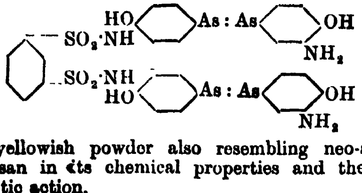
The product is a pale-yellow powder giving a neutral aqueous solution. Its curative effect closely resembles that of salvarsan. The *phosphamic* acid derivative of salvarsan, first prepared by Mouneyrat, is also an acidic substance yielding neutral solutions in aqueous sodium carbonate. It is known as *Galyl* (No. 1116 of Mouneyrat's series), and its constitution is as follows:—



(4 : *4′-Dihydroxyarsenobenzene*-3 : *3′-phosphamic acid*).

Ludyl (' 1151 ' of Mouneyrat's series).

Benzene-m-3′ : *3′-disulphamino-bis-3-amino*-4 : *4′-dihydroxyarsenobenzene*



a yellowish powder also resembling neo-salvarsan in its chemical properties and therapeutic action.

Co-ordination compounds of metals with arsenoaryl compounds were first discovered and investigated by Ehrlich, who made known his results at the International Congress of Medicine held in London in 1913. Danysz shortly afterwards made similar observations, and since the first communication was made a very large number of these complexes have been prepared and examined. The arsenoaryls giving the best results so far are arsenobenzene, salvarsan, and neosalvarsan, and of these the copper co-ordination compounds are isolated most readily, whilst the silver co-ordination compounds show the greater promise in therapeutics.

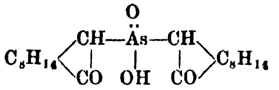
The most important of these compounds so far produced is that derived from salvarsan, silver bromide, and antimony. It is the silver bromide antimonyl sulphate co-ordination compound of salvarsan having the formula:

$$[C_{12}H_{12}O_2N_2As_2]_2AgBr,SbO(H_2SO_4)_2.$$

The name *Luargol* has been given to this substance, and it promises to be very efficacious in protozoal diseases, having much more marked trypanocidal properties than salvarsan, with no increase in toxicity. Luargol is insoluble in water, and is rendered soluble by caustic soda (0·4 gram of NaOH to 1·0 gram of drug). It is preferably injected intravenously, ill-effects are produced by subcutaneous application.

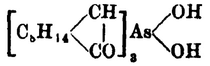
MISCELLANEOUS ORGANIC DERIVATIVES OF ARSENIC.

Dicamphorylarsinic acid



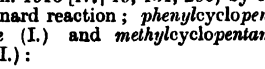
A condensation product of sodium, camphor and arsenic trichloride, consists of colourless transparent prisms; m p. 266° (with decomposition); $[\alpha]_D^{20}+186{\cdot}6°$; practically insoluble in water or petroleum, more soluble in benzene, freely soluble in chloroform or alcohol (Morgan and Micklethwait, Chem. Soc. Trans. 1908, 93, 2146; 1909, 95, 1476; Morgan and Moore, Chem. Soc. Trans. 1910, 97, 1699).

Tricamphorylarsinic acid



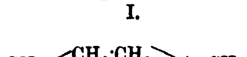
is obtained from the final mother liquors of the above preparation after systematic fractionation, the ultimate product being a brown amorphous solid very soluble in benzene, alcohol, or acetic acid, and recovered from these solvents as a viscid mass (Morgan and Micklethwait, *l.c.*).

Cyclic derivatives of arsenic have been obtained recently (Grüttner and Wiernik, Ber. 1915, 48, 1473; 1916, 49, 437; Lappe, Bull. Soc. chim. 1916 [iv,] 19, 151, 290) by employing the Grignard reaction; *phenyl*cyclo*pentamethylenearsine* (I.) and *methyl*cyclo*pentamethylenearsine* (II.):



$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>As\cdot C_6H_5$$

I.

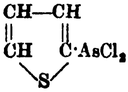


$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>As\cdot CH_3$$

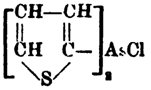
II.

Arsenical derivatives of thiophen may be synthesised by the use of organo-mercury compounds as employed by Michaelis in his earlier work (Michaelis, Annalen, 1880, 201, 196; 1902, 320, 272).

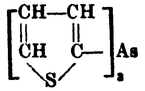
Thienylarsenious chloride (I.), *Dithienylarsenious chloride* (II.), and *Trithienylarsine* (III.):



I.



II.



III.

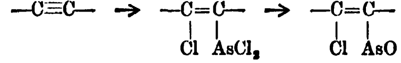
are obtained as successive fractions from the filtrate when arsenious chloride and mercuridithienyl are allowed to react under carefully regulated conditions (Steinkopf, with Banermeister, Annalen, 1917, 413, 331).

This reaction was first studied by Finze and Furlotti (Gazz. chim. ital. 1915 [ii.] 45, 280, 290 who oxidised the two chloro- compounds to the corresponding *thienylarsinic* and *dithienylarsinic acids*.

Strontium chloroarsinobehenolate

$$Sr(C_{22}H_{39}O_3AsCl)_2,$$

a colourless amorphous precipitate introduced into pharmacy under the name of *Elarson*, and giving good clinical results in anæmia, is prepared by heating together behenolic acid and arsenious chloride at 140°, the additive compound being then treated successively with aqueous caustic alkali and methyl-alcoholic strontium chloride containing ammonia. In this process arsenious chloride is added to the triple linking of behenolic acid (E Fischer, Annalen, 1914, 403, 109)



$$-C\equiv C- \rightarrow -\underset{\displaystyle Cl}{\underset{|}{C}}=\underset{\displaystyle AsCl_2}{\underset{|}{C}}- \rightarrow -\underset{\displaystyle Cl}{\underset{|}{C}}=\underset{\displaystyle AsO}{\underset{|}{C}}-$$

Protein combinations containing arsenic.—Insoluble combinations containing firmly attached arsenic which does not give the ordinary analytical reactions of the element are produced by dissolving albumin from white of egg in acetic anhydride, and by adding successively to the solution phosphoric anhydride and arsenious chloride. The protein precipitate is freed from phosphoric and arsenious acids by washing with water (Guezda, D. R. P. 201370).

Arsenical preparations insoluble in the gastric juices are produced by adding arsenious chloride to gliadin or glutenin suspended in alcohol. The final product is soluble in hot water and contains 4·3 p.c. of arsenic (D. R. P. 214717).

Soluble stable combinations of salvarsan base and proteins have been recommended for use in therapeutics (D. R. P. 261542); they are prepared by dissolving in alkali the additive compounds of salvarsan, and the alkali salts of lysalbic and protalbic acids or similar protein acids. The reacting alkali salts are precipitated by alcohol-ether or obtained by concentration *in vacuô*.

THE USE OF ORGANIC ARSENICALS IN CHEMICAL WARFARE.

The organic arsenicals chiefly employed in the chemical offensive of the Great War were aromatic arsenicals containing tervalent arsenic. These compounds had very disagreeable physiological properties and functioned as lachrymators, sternutators and respiratory irritants. *Diphenylarsenious chloride* (*diphenylchloroarsine*) possessed these irritating properties in a very marked degree. It was prepared for this purpose by heating triphenylarsine (2 mols.) and arsenious chloride (1 mol.) at 300° in autoclaves. The by-product of this reaction, *phenylarsenious chloride*, was also a respiratory irritant and had a vesicating action on the skin. It was separated by fractional distillation from diphenylarsenious chloride.

Alternatively phenylarsinic acid was prepared from sodium arsenite and benzenediazonium chloride in presence of copper sulphate (Bart's reaction). This acid, reduced with sulphurous acid in the presence of hydrochloric acid, gave rise to phenylarsenious chloride. The latter compound dissolved in aqueous sodium hydroxide and treated with benzenediazonium chloride furnished diphenylarsinic acid, which on reduction with sulphurous and hydrochloric acids yielded diphenylarsenious chloride. The overall yield by these processes varied between 24 and 36 per cent. The foregoing repetition of the Bart reaction was avoided by a combination of the Michaelis and Bart method leading to diphenyl-arsenious chloride when triphenylarsine is heated to 300° with phenylarsenious chloride.

Diphenylarsenious cyanide $(C_6H_5)_2As\cdot CN$, of which large quantities were employed in the later stages of the war, was manufactured by digesting diphenylarsenious chloride with a warm concentrated aqueous solution of sodium or potassium cyanide. It was obtained in colourless crystals melting at 31°.

The aromatic arsenicals containing quinquevalent arsenic, such as triphenylarsine dichloride, when vapourised by heat, behaved as sternutators and respiratory irritants; but this effect was probably due to the formation of compounds of tervalent arsenic akin to diphenylarsenious chloride. The corresponding organic antimonials, although irritant and lethal, offered no advantages over the aromatic arsenicals.

The aliphatic arsenicals of the cacodyl and alkyl arsenious chloride series were found to be respiratory irritants and lethal agents, methylarsenious chloride, ethylarsenious chloride and cacodyl cyanide being among the most toxic. Methylarsenious chloride was manufactured in America by methylating sodium arsenite with dimethyl sulphate, reducing the resulting sodium methylarsinate to methylarsenious oxide, and treating this oxide with hydrogen chloride. Ethylarsenious chloride, manufactured at Höchst and Ludwigshafen, was prepared by a similar series of processes, starting from sodium arsenite and ethyl chloride (Journ. Indust. Engin. Clem. 1919, 11, 105, 826). But on the whole these aliphatic derivatives were not more effective in producing casualties than the above-described aromatic arsenicals.

Bibliography.—Organic Compounds of Arsenic and Antimony, G. T. Morgan. London. 1918. Handbuch der Organischen Arsenverbindungen, A. Bertheim. Stuttgart. 1913. Die Aromatische Arsenverbindungen, H. Schmidt.

Berlin. 1912. Dir Arzneimittel Synthese, S. Fraenkel. Berlin. 1912, 603. Salvarsan or '606' (Dioxydiaminoarsenobenzol). Its Chemistry, Pharmacy, and Therapeutics. (W. H. Martindale. London. 1911.) Chimie et toxicologie de l'arsenic et de ses composes.' A Valeure. Paris. 1904. G. T. M.

ARGATOXYL. Silver-*p*-aminophenyl arsenate.

ARGOCHROM. Silver methylene blue.

ARSALYTE. Dimethyl amino tetramido arsenobenzene.

ARSAMINAL. Japanese name for salvarsan.

ARSENICAL PYRITES or *Arsenical mundic.* Names commonly used by miners for the mineral *mispickel* (*q.v.*) or *arsenopyrite* (FeAS), which is the principal ore of arsenic.

ARSENIC MOULD. *Penicillium brevicaule.* This organism, first obtained by Gosio, in presence of an arsenic compound, forms *diethylarsine* $AsH(C_2H_5)_2$, to which the poisonous gas developed by wall-papers containing arsenic is probably due. The formation of diethylarsine by the action of this mould has been used as a test for arsenic by Markmann (Chem. Zentr 1900, ii. 1187); Galli-Valerio and Strzyzowski (*ibid.* 1901, i. 63).

Penicillium brevicaule also gives garlic or mercaptan-like odours with compounds of selenium and tellurium (Maassen, Chem. Zentr. 1902, i. 1245).

ARSENOFERRATIN. Sodium arseno-ferri-albuminate.

ARSENOGENE. Trade name for an albuminous preparation of arsenic and iron obtained by heating peptonised casein with arsenic acid and ferric ammonium sulphate. Used in medicine (Salkowski, Apoth. Zeit. 1908, 23, 114).

ARSENOPYRITE *v.* Mispickel.

ARSENOTRIFERRIN. Iron arseno-*p*-nucleinate.

ARSEN-PHENOLAMINE. Syn. for salvarsan. *See* Arsenicals, Organic.

ARSINE. *Arsenic trihydride* (*v.* Arsenic).

ARSINOSOLVINE. Sodium salt of amino phenylarsenic acid.

ARSPHENAMINE. U.S. Pharm. title for salvarsan.

ARTARINE $C_{21}H_{23}O_4N$, m.p. 240°, is an amorphous alkaloid from Ar ar-root of *Xanthoxylon senegalense.* The hydrochloride $B,HCl,4H_2O$ forms yellow needles, very little soluble in water (Giacosa and Soave, Gazz. chim. ital. 1889, 19, 303).

ARTEMISIN. An alkaloid isolated by Merck from the mother liquors obtained in the preparation of santonin from the seeds of *Artemisia maritima.* Forms colourless crystals; m.p. 200°; sparingly soluble in water, more soluble in alcohol; $[\alpha]_D -84{\cdot}3°$. With hot soda solution gives a carmine-red solution, colourless on cooling. Gives an oxime with hydroxylamine, and a hydrazone with phenylhydrazine (Bertolo, Pharm. J. 1902, 489; Freund and Mai, Ber. 1901, 3717; *cf.* Wedekind and Koch, Ber. 1905, 1845)(*v.* Santonica).

ARTERENOL. Trade name for *o*-Dihydroxyphenylaminomethyl carbinol hydrochloride. *V.* Adrenaline.

ARTICHOKE. Three vegetables are known by this name: (1) the Globe artichoke—the flower head of *Cynara scolymus*; (2) the Jerusalem artichoke—the tuber of *Helianthus tuberosus*; (3) the Japanese or Chinese artichoke—called also Chorogi—the tuber of *Stachys tuberifera.*

The following are analyses of the tubers of the two latter:—

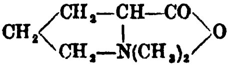
	Water	Protein	Fat	Carbohydrates	Ash
Jerusalem artichoke . .	79·5	2·6	0·2	16·7	1·0
Stachys tuberifera	78·05	4·32	0·16	14·63	1·21

(Strohmer and Stift, Bied. Zentr. 21, 820.)

The 'protein' of the Jerusalem artichoke includes much material other than true proteid; the carbohydrates consist largely of inulin and levulin.

According to Tanret (Compt. rend. 1893, 117, 50), two other carbohydrates—*helianthenin* m.p. 176°, $12C_6H_{10}O_5+3H_2O$, and *synanthrin*, m.p. 170°, $8C_6H_{10}O_5+H_2O$—are also present, and the levulin or synanthrose described by other observers as occurring in artichokes, is a mixture of saccharose and synanthrin.

The tubers of *Stachys tuberifera* contain many nitrogenous substances of an amide nature—*glutamine, tyrosine, arginine, choline, trigonelline,* and the characteristic body, *stachydrine*



The amount of the last-named is estimated at 0·18 p.c. of the dry substance (Schulze and Trier, Zeitsch. physiol. Chem. 1910, 67, 59). The characteristic carbohydrate is *stachyose* $C_{18}H_{32}O_{16},3H_2O$ (*q.v.*). H. I.

ARTOCARPUS BARK. The inner bark (bast) of the bread-fruit tree [*A. incisa* (Linn.)] is used by the South Sea Islanders for making ropes and clothing. According to Moeller (Dingl. poly. J. 231, 463), this fibre would probably be a very useful one. It can be obtained in large quantities.

ARTOCARPUS INTEGRIFOLIA (Linn. f.). (*Jack Tree*) *v.* Jackwood; Dyes, Natural.

ARUM MACULATUM (Linn.). The common arum, 'wake robin,' or 'lords and ladies,' 'cows and calves,' formerly known as 'abron' janus, 'ramp,' 'starch wort,' contains a starch which was made into a kind of arrowroot in the Isle of Portland, and was the active ingredient of 'Portland powder,' a so-called specific for gout. Occasionally sold in Paris as a cosmetic, under the name of *poudre de Cypre.*

Amorphophallus campanulatus (Blume) is used in India as a vegetable and also in medicine, as are other of the Arums. Many of the Aroideæ act as poisons, their toxic action being due apparently to the irritation induced by the raphides contained in the cells (Pedler and Warden, Jour. Asiatic Soc. of Bengal, 57, 2, 106; Stahl; Pflanzen und Schnecken, Zeitsch. Nat. u. Med. Jena, xxii. N. F. xv. 1888).

ASAFŒTIDA *v.* Gum resins.

ASAPROL *v.* Abrastol.

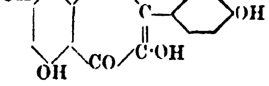
ASARUM CANADENSE (Linn.). A plant indigenous to North America, where it is known by the names of 'Wild Ginger,' or 'Canada Snake-root.' The rhizome yields on distillation an essential oil used in perfumery, containing a phenol $C_9H_{12}O_2$, *d-* and *l-* pinene, *d*-linalool, -borneol, *l*-terpineol, geraniol, eugenol methyl ether, a lactone $C_{14}H_{26}O_2$, a mixture of fatty acids, including palmitic and acetic, and a blue oil of undetermined composition, consisting of oxygenated substances of alcoholic nature (Power and Seed, Chem. Soc. Trans. 1902, 81, 59).

ASBARG. Asbarg consists of the dried flowers and flowering stems of the *Delphinium zalil*, which is found in great quantity in Afghanistan. The dyestuff is collected and taken to Multan and other Punjab towns, from which it is conveyed all over India. It is or was much used in silk-dyeing for the production of a sulphur-yellow colour known as 'gandkaki,' and, together with *Datisca cannabina*, to obtain a similar shade on alum-mordanted silk; it is also used in calico-printing. The flowers, which are bitter, are likewise employed medicinally as a febrifuge.

The colouring matters of asbarg are present entirely as glucosides, and are best isolated in the crude condition by digesting the boiling aqueous extract with a little sulphuric acid (Perkin and Pilgrim, Chem. Soc. Trans. 1898, 268). A brownish-yellow powder thus separates, which contains three substances: *isorhamnetin*, *quercetin*, and *kaempferol*.

Iso*rhamnetin* $C_{16}H_{12}O_7$, the sparingly soluble constituent, forms yellow needles, resembling rhamnetin in appearance. With lead acetate in alcoholic solution, an orange-red precipitate is formed, whilst ferric chloride gives a greenish-black colouration. Fused with alkali, *phloroglucinol* and *protocatechuic acid* are produced, and when air is aspirated through its alkaline solution, *phloroglucinol* and *vanillic acid* are obtained.

With acetic anhydride *iso*rhamnetin gives a *tetra-acetyl* derivative $C_{16}H_8O_7(C_2H_3O)_4$, colourless needles, m.p. 195°–196°; and with methyl iodide a *trimethyl ether*, which is identical with *quercetin tetramethyl ether*. As, moreover, by the action of hydriodic acid *iso*rhamnetin yields quercetin, its constitution can only be represented as follows:—



The dyeing properties of *iso*rhamnetin are similar in character to those given by kaempferol. *iso*Rhamnetin is also present in yellow wallflowers (*Cheiranthus cheiri*) (Perkin and Hummel), and in red clover flowers, *Trifolium pratense* (Power and Salway, Chem. Soc. Trans. 1910, 97, 245). A description of the more soluble colouring matters quercetin (*quercitron bark*) and kaempferol (*Delphinium consolida*) is given elsewhere.

In dyeing properties asbarg closely resembles quercitron bark, but yields with aluminium mordant a purer or less orange-yellow. It is, however, a much weaker dyestuff, having but 35 p.c. the dyeing power of quercitron bark. The colouring matter of the flowers, apart from the flowering stalks, is present to the extent of 3·47 p.c.

The stems and flowers of the *D. saniculæfolium* gives shades analogous to, though somewhat weaker than, those yielded by the *D. zalil*.

A. G. P.

ASBESTOS, from ἄσβεστος, 'unquenched.' Both in ancient and modern times various silicate minerals, closely resembling one another in their finely fibrous texture and flexibility, have been and are still confused under this name. The same is true also of the name 'amianthus' or 'aminatos' (ἀμίαντος, 'undefiled,' because not injured by fire). They are, therefore, collective names of no more definite signification than the adjective 'asbestiform.' Mineralogists are, however, agreed in limiting the name asbestos to the fibrous forms of hornblende, but this limitation is not generally observed. Any ambiguity may be avoided by using the terms amphibole-asbestos (or hornblende-asbestos), serpentine-asbestos, &c., for these asbestiform minerals. The finely fibrous texture is, of course, an accidental character of the mineral species, depending on the enormous elongation in one direction of the individual crystals which form the aggregate. Such a character might, indeed, be assumed by many kinds of minerals; but it is only the following that are of any importance in this connection:—

Tremolite, $CaMg_3(SiO_3)_4$.
Actinolite, $Ca(Mg,Fe)_3(SiO_3)_4$.
Crocidolite, $NaFe'''(SiO_3)_2 \cdot Fe''SiO_3$.
Anthophyllite, $(Mg,Fe)SiO_3$.
Serpentine, $H_4Mg_3Si_2O_9$.
Palygorskite group (pilolite, &c.), $\left\{ \begin{array}{l} nH_8Mg_2Si_3O_{12} \\ mH_2Al_2Si_4O_{12}, 5H_2O. \end{array} \right.$

The first two of these differ only in the relative proportions of the mutually replaceable magnesium and ferrous iron (and consequently also in their colours, which are white and green respectively), and they are merely varieties of the species amphibole or hornblende. Crocidolite is another species of the amphibole group of minerals, crystallising in the monoclinic system, and also with an angle of 56° between its prismatic cleavages. It is known in the trade as 'blue asbestos,' and it gives the name to the Asbestos Mountains in South Africa, where it is found. Whilst hornblende is more frequently found as stout crystals and compact masses, crocidolite, on the other hand, is as yet known only in the finely fibrous form. Anthophyllite also belongs to the amphibole group, but is orthorhombic in crystallisation. Some of the asbestos mined in the United States (Georgia and Idaho) is of this kind. Serpentine occurs in nature as large rock-masses, and the compact rock is frequently traversed by veins of fibrous material of the same composition; the latter is known to mineralogists as *chrysotile*, and in the trade as 'asbestos' or 'Canadian asbestos.' In the minerals of the palygorskite group (A. E. Fersman, Bull. Acad. Sci. St. Petersburg, 1908, ii, 255, 637) the fibres rarely show a parallel arrangement, but are more usually matted and interwoven, giving felted masses known as 'mountain-leather,' 'mountain-cork,' and 'mountain-wood.' It is, however, to be remembered that these trivial names may also be applied to similar aggregates of fibrous amphibole.

From a practical point of view, the most important of these are *tremolite-asbestos* and *serpentine-asbestos*, which in the trade are known as 'Italian asbestos' and 'Canadian asbestos' respectively. The former is met with as aggregates or bundles of white or greyish fibres, sometimes several feet in length, usually arranged parallel to the surfaces of crevices in the metamorphic and crystalline rocks of mountainous districts. It is mined in the Alps, Urals, and Appalachians. The supply is limited and uncertain, and the hardness of the enclosing rocks makes mining difficult. The principal mines are those in the north of Italy, in the Susa and Aosta valleys in Piedmont, and the Valtellina in Lombardy. These are, however, now of little importance, since the use of hornblende-asbestos has been largely replaced by serpentine-asbestos.

Serpentine-asbestos, or chrysotile, occurs in small veins forming an irregular network in serpentine-rock. It has in the closely compacted mass an oil-yellow or greenish colour with a pronounced silky lustre and a certain degree of translucency. When rubbed or crushed, it readily separates into white cottony fibres (pierre à coton of the French-Canadians). The fibres are arranged perpendicularly to the walls of the vein, and are usually only an inch or two in length, never exceeding 6 inches. The mineral usually contains 2-3 p.c. FeO isomorphously replacing magnesia. Chrysolite is found at all the localities where serpentine-rock occurs (*e.g.* the Lizard district in Cornwall), and it is extensively mined in Canada, Russia, South Africa, and the United States. Of these the most important are the Canadian deposits, which have been worked since 1878. The mining districts are near the villages of Thetford, Black Lake, East Broughton, and Danville in Quebec; and extend over the United States border into Vermont. The mineral is also mined in Arizona and California. In Russia, the principal deposits are in the Ural Mountains, in the neighbourhood of Ekaterinburg and Orenburg; and there are others in the Caucasus. Recently, rich deposits have been opened up in Rhodesia in the Victoria and the Gwelo districts, and in the Caroline district in the Transvaal. The asbestos quarried by the ancients at Karystos in Eubœa (Karystian stone), and in Cyprus, was also a serpentine-asbestos (J. W. Evans, Mineral. Mag. 1906, xiv, 143; Geol. Mag. 1909, vi, 286). He suggests the name *Karystiolite* as an alternative for chrysotile, owing to its confusion with chrysolite—a synonym of olivine). It was used for wicks in the perpetually burning lamps of the temples; and was woven into napkins, which could be cleansed by fire, and into cremation shrouds.

The blue asbestos or crocidolite (*q.v.*) of South Africa has during the last twenty years become of commercial importance and has been mined in increasingly large amounts. It occurs as layers interbedded in the brown jaspers and ironstones of the lower portion of the Pretoria series of sedimentary rocks, and is quarried or mined as slabs in which the fibres of the mineral run perpendicularly or somewhat obliquely to the surfaces. The belt of crocidolite-bearing rocks extends for a distance of about 300 miles, with a width of 4–20 miles, from the Orange River through the Asbestos Mountains in Griqualand West into Bechuana Land. Beautiful silky, loose fibrous material is known from Cochabamba in Bolivia.

These various kinds of asbestos differ somewhat in their resistance to acids and heat. Chrysotile is decomposed by hydrochloric and sulphuric acids; at a red heat (but not below) it loses water, and the fibres can be fused in the bunsen-flame. Tremolite-asbestos is not attacked by acids, and it is more difficultly fusible. On the other hand, the fibres of chrysotile are more flexible and more suitable for textile purposes. Crocidolite is readily fusible to a black magnetic glass, but it has the advantage that it is but slightly attacked by acids, chemical solutions, and sea-water. It possesses a greater tensile strength and is more elastic than chrysotile; and is further a good insulator for heat and electricity. Notwithstanding these differences, these varieties of asbestos are put to much the same uses, but serpentine-asbestos is employed in far larger quantities.

Spun asbestos is largely used for steam packings, fireproof curtains; and as cloth, twine, and rope it finds a variety of applications. As an insulating material, asbestos fibre is used for coating steam and hot-water pipes and cold-storage plants; and as a lining in safes, stoves, and furnaces. For use as a constructional fireproof material, it is made into bricks, boards, millboards, plasters, and paints, being often mixed with other materials. The so-called 'asbestic,' largely used for wall plaster, is prepared by grinding the poorer material and waste, which consists of narrow veins of asbestos still enclosed in the serpentine-rock. In the laboratory, asbestos is used for filtering (a pure white tremolite-asbestos being best for this purpose), for stoppings in combustion tubes, and in the form of card for supports. Asbestos paper or twine, soaked in sodium silicate and afterwards treated with calcium chloride solution, can be used for repairing glass apparatus.

References.—F. Cirkel, Chrysotile-asbestos, its Occurrence, Exploitation, Milling, and Uses (Mines Branch, Ottawa, end edit., 1910); R. H. Jones, Asbestos (London, 1890), and Asbestos and Asbestic (London, 1897); G. P. Merrill, Asbestos and other Asbestiform Minerals (Proc. U. S. Nat. Museum, 1895, xviii, 281), and Non-metallic Minerals (New York, 1910); H. Ries, Economic Geology (New York, 1916); Production and Uses of Asbestos (Bull. Imp. Inst. 1905, iii, 277); The Technical Preparation of Asbestos (*ibid.* 1908, vi, 393); J. S. Diller. Mineral Resources of the United States, for 1915, 1916, ii, 13; H. F. Olds, Blue Asbestos [Crocidolite in South Africa] (Trans. Inst. Mining and Metall. 1899, vii, 122); O. B. Hopkins, Mineral Industry (New York, 1916, 1917, xxv, 62); and Bull. Geol. Survey, Georgia, 1914, No. 29; G. E. B. Frood, The Cape Asbestos Industry [Crocidolite] (Ann. Rep. Govt. Mining Engineer, Dept. of Mines, S. Africa, 1915; and S. African Mining Journ. 1916); P. A. Wagner, Asbestos in South Africa, (S. African Journ. of Industries, 1917, i, No. 3); A. L. Hall, Asbestos in the Union of South Africa (Geol. Survey, 1918, Mem. No. 12). For an account of the Canadian asbestos industry, *see* J. Roy. Soc. Arts, 1913, 62, 36).

L. J. S

ASDUANA *v.* BRIDELIA BARK.

ASEPTIN. Trade name for a mixture of hydrogen peroxide, boric acid, and salicylic acid; used as an antiseptic.

ASEPTOL. Trade name originally given to a solution of *o*-phenolsulphonic acid $C_6H_4(OH)SO_3H$. It is a thick reddish fluid, of 1·45 sp.gr., having a faint odour like phenol. Occasionally called *sozolic acid*. It is an antiseptic, but does not possess the poisonous action peculiar to phenol, and is therefore recommended for surgical and ophthalmic operations (Chem. Zentr. 1884, 720).

The aseptol of Merck is *p*-phenol sulphonic acid mixed with about 6 p.c. of the *o*-acid (Obermiller, Chem. Zentr. 1907, 1615).

The name is also given to a preparation containing from 0·25 to 10 parts potassium oxyquinoline sulphate, 0·5 to 10 parts soap, dissolved in 1000 parts of water, mixed with terpineol or other aromatic substances, and occasionally glycerol (Pharm. Zeit. 1897, 770).

Aseptol is also the name given to an ill-defined mixture of phenyl ethers and sulphonated phenols, obtained by the action of sulphuric acid on phenol in presence of alcohol (Trillat, J. Soc. Chem. Ind. 1892, 1028).

***ASFRAX** or *Tbayamanu*. An Indian drug, consisting of the flowers, flower-stalks, and immature fruit of a species of *Delphinium*. Used in Bombay as a medicine, and as a yellow dye for silk (Dymock, Pharm. J. [3] 8, 161).

ASH. This term is sometimes used to denote the inorganic or mineral matter contained in any substance, but more generally refers to the residue left on completely burning or incinerating it. The two meanings are not necessarily the same, since in any animal or vegetable substance the inorganic constituents are usually present in very different states of combination to those in which they occur in the residue left when the substance is completely oxidised.

To ascertain the exact amount and composition of the inorganic matter present in any organic substance is often a matter of considerable difficulty, and, in many cases, is impracticable.

The term 'ash' should be used, therefore, only in the second sense given above.

Most animal and vegetable substances leave, on combustion, a residue containing the following constituents in varying proportions :—

Acidic	Basic
Chlorine	Sodium
Carbon dioxide	Potassium
Sulphur trioxide	Calcium
Sulphur	Magnesium
Phosphorus pentoxide	Iron
Silica	Manganese

Other constituents, generally in small quantities, are also often present.

In the original substance the greater portions of the basic constituents in the above list are probably present in combination with organic acids, and, consequently, are left in the ash as carbonates (often largely the case with potash and soda) or as oxides (*e.g.* portions of the lime, magnesia, oxides of iron, and manganese) ; while the carbonates, sulphates, and phosphates are, in many cases, derived from organic combinations of carbon, sulphur, and phosphorus existing in the original substance. The determination of the amount and composition of the ash of animal and vegetable substances, though, perhaps, inadequate to ascertain the exact nature of the inorganic constituents of the organised bodies, affords valuable information as to their fitness as foodstuffs, and as to the needs of animals or plants.

In the process of incineration, there is great danger of loss of chlorides of potassium and sodium by volatilisation, also of reduction of phosphates and sulphates by the reducing action of the hot carbon. Berthelot proposed to overcome these difficulties by heating in a current of oxygen, the substance to be incinerated being previously mixed with a known weight of sodium carbonate (Compt. rend. 128, 23 ; *cf.* Roberts, Analyst, 1918, 254).

Shuttleworth (Chem. Zentr. 1899, ii. 114) has suggested the addition of calcium acetate in order to prevent the sintering which is so often an obstacle to complete incineration, and has devised a special platinum vessel in order to prevent loss of chlorides by volatilisation, and to hasten incineration. A modified form of this apparatus is described by Tucker (Ber. 32, 2583).

A convenient method of minimising the loss of chlorides by volatilisation is to char the substance thoroughly at a moderate temperature, then cool and extract the black residue with water, filter off the soluble matter, and complete the incineration of the residue after drying. When all black particles have disappeared, the residue is allowed to cool, the aqueous extract added, evaporated to dryness, and then moderately heated. Addition of ammonium nitrate to the black char hastens the combustion of the carbon.

Ash of animals. The proportion of ash constituents present in the whole body of an animal depends largely upon its condition, being greater in lean than in fat animals. According to the Rothamsted experiments, the following table gives the average proportions of ash and of its main constituents in the whole bodies of various farm animals in a fatted condition :—

—	Total ash	Phosphoric acid P_2O_5	Lime CaO	Magnesia MgO	Potash K_2O
Fat calf .	3·9	1·54	1·65	0·08	0·21
Half-fat ox .	5·1	1·84	2·11	0·09	0·21
Fat ox . .	4·2	1·55	1·79	0·06	0·18
Fat lamb .	3·2	1·13	1·28	0·05	0·17
Store sheep .	3·3	1·19	1·32	0·06	0·17
Fat sheep .	3·0	1·04	1·18	0·05	0·15
Store pig .	2·8	1·07	1·08	0·05	0·20
Fat pig .	1·7	0·65	0·64	0·03	0·14

The other constituents of the ash consist chiefly of sodium, chlorine, fluorine, iron, manganese, iodine, and silica.

The bones and teeth contain the greater part of the phosphoric acid, lime, magnesia, and fluorine; potash is present largely in muscle, blood, and many of the secretions; sodium, chlorine and iron are largely present in the blood and the secretions, while iodine is mainly accumulated in the thyroid gland.

(For the amount and composition of the ash

The following table, compiled chiefly from Wolff's analyses, gives the average proportions of ash and of its chief components in various fresh or air-dried agricultural products.

100 parts of the substance contain:—

Substance	Water	Ash	K_2O	Na_2O	MgO	CaO	P_2O_5	SO_3	SiO_2	Cl	S
I. *Green Fodder.*											
Meadow grass	70·0	2·33	0·60	0·16	0·11	0·27	0·15	0·12	0·69	0·19	0·06
Rye grass	70·0	2·13	0·53	0·09	0·05	0·16	0·17	0·08	0·84	0·11	0·07
Timothy grass	70·0	2·10	0·61	0·06	0·08	0·20	0·23	0·08	0·75	0·11	0·08
Oats, in blossom	77·0	1·66	0·65	0·06	0·05	0·11	0·14	0·05	0·55	0·07	0·04
Barley, „	68·0	2·25	0·59	0·01	0·07	0·14	0·22	0·07	1·08	0·08	0·07
Wheat, „	69·0	2·17	0·56	0·01	0·05	0·07	0·16	0·04	1·23	0·06	0·05
Rye fodder	70·0	1·63	0·63	0·01	0·05	0·12	0·24	0·02	0·52	—	—
Red clover	80·0	1·34	0·46	0·02	0·16	0·46	0·13	0·04	0·04	0·05	0·05
White clover	81·0	1·36	0·24	0·11	0·14	0·44	0·20	0·12	0·06	0·04	0·06
Lucerne	75·3	1·76	0·45	0·02	0·10	0·85	0·15	0·11	0·04	0·03	0·08
Sainfoin	78·5	1·16	0·46	0·02	0·07	0·37	0·12	0·04	0·05	0·03	—
Green vetches	82·0	1·57	0·66	0·05	0·11	0·41	0·20	0·06	0·03	0·05	0·03
Potato tops	77·0	1·18	0·07	0·01	0·27	0·55	0·06	0·06	0·05	0·04	0·05
Mangold tops	90·7	1·48	0·43	0·31	0·14	0·17	0·08	0·11	0·07	0·17	0·05
Sugar-beet tops	89·7	1·80	0·40	0·30	0·33	0·36	0·13	0·14	0·06	0·10	—
Turnip tops	89·8	1·40	0·32	0·11	0·06	0·45	0·13	0·14	0·05	0·12	0·05
Chicory tops	85·0	1·87	1·12	0·01	0·06	0·27	0·17	0·17	0·02	0·03	—
Carrot tops	80·8	2·61	0·37	0·60	0·12	0·86	0·12	0·21	0·15	0·19	0·14
Cabbage heads	88·5	1·24	0·60	0·05	0·04	0·19	0·20	0·11	0·01	0·03	0·05
Kohl-rabi tops	85·0	2·53	0·36	0·10	0·10	0·84	0·26	0·30	0·26	0·10	—
II. *Hay and Straw.*											
Meadow hay	14·4	6·66	1·71	0·47	0·33	0·77	0·41	0·34	1·97	0·53	0·17
Red clover hay	16·0	5·65	1·95	0·09	0·69	1·92	0·56	0·17	0·15	0·21	0·21
White clover hay	16·0	6·03	1·06	0·47	0·60	1·94	0·85	0·53	0·27	0·19	0·27
Lucerne hay	16·0	6·00	1·52	0·07	0·35	2·88	0·51	0·37	0·12	0·11	0·26
Sainfoin hay	16·0	4·53	1·79	0·08	0·26	1·46	0·47	0·15	0·18	0·14	—
Oat hay	14·5	6·18	2·41	0·20	0·20	0·41	0·51	0·17	2·05	0·25	0·15
Wheat straw	14·1	4·26	0·49	0·12	0·11	0·26	0·23	0·12	2·82	—	0·16
Rye straw	15·4	4·07	0·76	0·13	0·13	0·31	0·19	0·08	2·37	—	0·09
Barley straw	14·0	4·39	0·93	0·20	0·11	0·33	0·19	0·16	2·36	—	0·13
Oat straw	14·1	4·40	0·97	0·23	0·18	0·36	0·18	0·15	2·11	—	0·17
Maize straw	14·0	4·72	1·66	0·05	0·26	0·50	0·38	0·25	1·79	—	0·39
Pea straw	14·3	4·92	1·07	0·26	0·38	1·86	0·38	0·28	0·28	0·30	0·07
Field bean straw	18·0	5·84	2·59	0·22	0·46	1·35	0·41	0·01	0·31	0·81	0·22
Buckwheat straw	16·0	5·17	2·41	0·11	0·19	0·95	0·61	0·27	0·28	0·40	—
Flax straw	14·0	3·19	1·18	0·16	0·23	0·83	0·43	0·20	0·22	0·15	0·14
Flax, whole plant	25·0	3·23	1·13	0·15	0·29	0·50	0·74	0·16	0·08	0·19	—
Hop, „ „	25·0	7·40	1·94	0·28	0·43	1·18	0·90	0·38	1·59	0·34	0·20
Hops	12·0	5·98	2·23	0·13	0·21	1·01	0·90	0·16	0·92	0·02	0·48
Tobacco	18·0	19·75	5·41	0·73	2·07	7·31	0·71	0·77	1·92	0·88	—
Heather	20·0	3·61	0·48	0·19	0·30	0·68	0·18	0·16	1·27	0·08	—
Broom	16·0	4·89	0·69	0·05	0·28	0·32	0·16	0·07	0·19	0·05	—
Fern	16·0	5·89	2·52	0·27	0·45	0·83	0·57	0·30	0·36	0·60	—
Reeds	18·0	3·85	0·33	0·01	0·05	0·23	0·08	0·11	2·75	—	—
Sedge	14·0	6·95	2·31	0·51	0·29	0·37	0·47	0·23	2·18	0·39	—
Rush	14·0	4·56	1·67	0·30	0·29	0·43	0·29	0·40	0·50	0·65	—
III. *Root Crops.*											
Potato	75·0	0·94	0·56	0·01	0·04	0·02	0·18	0·06	0·02	0·03	0·02
Artichoke	80·0	1·03	0·67	—	0·03	0·04	0·16	0·03	—	0·02	—
Mangold	88·3	0·80	0·43	0·12	0·04	0·04	0·08	0·03	0·02	0·05	0·02
Sugar beet	81·6	0·80	0·40	0·08	0·07	0·05	0·11	0·04	0·03	0·02	—
Turnip	90·9	0·75	0·30	0·08	0·03	0·08	0·10	0·11	0·02	0·03	0·04
White turnip	91·5	0·61	0·31	0·02	0·02	0·08	0·11	0·04	0·01	0·04	—
Kohl-rabi	87·7	0·95	0·49	0·06	0·02	0·09	0·14	0·08	0·01	0·05	—
Carrot	86·0	0·88	0·32	0·19	0·05	0·09	0·11	0·06	0·02	0·03	0·01
Chicory	80·0	1·04	0·42	0·08	0·07	0·09	0·15	0·10	0·06	0·04	—

Substance	Water	Ash	K_2O	Na_2O	MgO	CaO	P_2O_5	SO_3	SiO_2	Cl	S
IV. *Grains and Seeds.*											
Wheat	14·3	1·77	0·55	0·06	0·22	0·06	0·82	0·04	0·03	—	0·15
Rye	14·9	1·73	0·54	0·03	0·19	0·05	0·82	0·04	0·03	—	0·17
Barley	14·5	2·18	0·48	0·06	0·18	0·05	0·72	0·05	0·59	—	0·14
Oats	14·0	2·64	0·42	0·10	0·18	0·10	0·55	0·04	1·23	—	0·17
Spelt	14·8	3·58	0·62	0·06	0·21	0·09	0·72	0·06	1·58	—	—
Maize	13·6	1·23	0·33	0·02	0·18	0·03	0·55	0·01	0·03	—	0·12
Sorghum	14·0	1·60	0·42	0·05	0·24	0·02	0·81	—	0·12	—	—
Millet	13·0	3·90	0·47	0·04	0·33	0·04	0·91	0·01	2·05	—	0·18
Paddy rice	12·0	6·90	1·27	0·31	0·59	0·35	3·26	0·04	0·04	—	—
Rice	13·0	0·34	0·08	0·02	0·05	0·01	0·17	—	0·01	—	—
Buckwheat	14·1	0·92	0·21	0·06	0·12	0·03	0·44	0·02	—	0·02	—
Flax seed	11·8	3·22	1·04	0·06	0·42	0·27	1·30	0·04	0·01	—	0·17
Peas	13·8	2·42	0·98	0·09	0·19	0·12	0·88	0·08	0·02	0·06	0·24
Field beans	14·1	2·96	1·20	0·04	0·20	0·15	1·16	0·15	0·04	0·08	0·23
V. *Fruits, &c.*											
Apple, whole fruit	84·0	0·27	0·10	0·07	0·02	0·01	0·04	0·02	0·01	—	—
Pear, " "	80·0	0·41	0·22	0·04	0·02	0·03	0·06	0·02	0·01	—	—
Cherry, " "	78·0	0·43	0·22	0·01	0·02	0·03	0·07	0·02	0·04	0·01	—
Plum, " "	82·0	0·40	0·24	—	0·02	0·04	0·06	0·02	0·01	—	—
Acorns, fresh	56·0	0·96	0·62	0·01	0·05	0·07	0·16	0·05	0·02	0·01	—
Beech mast	18·0	2·71	0·62	0·27	0·31	0·67	0·56	0·06	0·05	0·01	—
Horse chestnuts	49·2	1·20	0·71	—	0·01	0·14	0·27	0·02	—	0·08	—
VI. *Leaves—Autumn.*											
Mulberry	67·0	1·17	0·23	—	0·06	0·30	0·12	0·01	0·41	—	—
Horse chestnut	60·0	3·01	0·59	—	0·24	1·22	0·25	0·05	0·42	0·12	—
Walnut	60·0	2·84	0·76	—	0·28	1·53	0·11	0·08	0·06	0·02	—
Beech	55·0	3·05	0·16	0·02	0·18	1·37	0·13	0·11	1·03	0·01	—
Oak	60·0	1·96	0·07	0·01	0·08	0·95	0·16	0·09	0·61	—	—
Scotch fir	55·0	0·63	0·06	—	0·06	0·26	0·13	0·03	0·08	0·03	—
Spruce	55·0	2·63	0·04	—	0·06	0·40	0·21	0·07	1·84	—	—
VII. *Manufactured Products.*											
Fine wheat flour	13·6	0·41	0·15	0·01	0·03	0·01	0·21	—	—	—	—
Wheat bran	13·5	5·56	1·33	0·03	0·94	0·26	2·88	—	0·06	—	—
Rye flour	14·2	1·69	0·65	0·03	0·14	0·02	0·85	—	—	—	—
Rye bran	13·1	7·14	1·93	0·09	1·13	0·25	3·42	—	—	—	—
Barley flour	14·0	2·00	0·58	0·05	0·27	0·06	0·95	0·06	—	—	—
Maize meal	14·0	0·95	0·27	0·03	0·14	0·06	0·43	—	—	—	—
Malt	4·2	2·66	0·46	—	0·22	0·10	1·07	—	0·88	—	—
Malt dust	9·2	5·96	2·08	—	0·08	0·09	1·25	0·38	1·77	—	—
Beer	90·0	0·39	0·15	0·03	0·02	0·01	0·13	0·01	0·04	0·01	—
Wine	86·6	0·28	0·18	—	0·02	0·02	0·05	0·01	0·01	—	—
Linseed cake	11·5	5·52	1·29	0·08	0·88	0·47	1·94	0·19	0·36	0·03	—
Cotton-seed cake	11·5	6·15	2·18	—	0·26	0·28	2·95	0·07	0·25	—	—
Potato skins	30·0	6·71	4·83	0·05	0·45	0·64	0·23	0·03	0·18	0·14	—
Buckwheat groats	14·0	0·62	0·16	0·04	0·08	0·01	0·30	0·01	—	0·01	—
VIII. *Wood (air-dried).*											
Apple tree	15·0	1·10	0·13	0·02	0·06	0·78	0·05	0·03	0·02	—	—
Beech, trunk	15·0	0·55	0·09	0·02	0·06	0·31	0·03	0·01	0·03	—	—
Beech, brushwood	15·0	1·23	0·17	0·03	0·13	0·59	0·15	0·01	0·12	—	—
Birch	15·0	0·26	0·03	0·02	0·02	0·15	0·02	—	0·01	—	—
Grape	15·0	2·34	0·70	0·16	0·16	0·87	0·30	0·06	0·02	0·02	—
Mulberry	15·0	1·37	0·09	0·20	0·08	0·78	0·03	0·14	0·05	0·06	—
Larch	15·0	0·27	0·04	0·02	0·07	0·07	0·01	0·01	0·01	—	—
Oak	15·0	0·51	0·05	0·02	0·02	0·37	0·03	0·01	0·01	—	—
Scotch fir	15·0	0·26	0·03	0·01	0·02	0·13	0·02	0·01	0·04	—	—

of various portions of the animal body, and of certain animal products, v. Bones; Blood; Milk; &c.)

A characteristic of the ash of animal substances in general, is the usual preponderance of lime over phosphorus pentoxide and the relatively high ratio of sodium to potassium.

Ash of plants. The nature of the ash of the leaves, stems, &c., of plants is affected to a considerable extent by the composition of the soil in which the plants grow, but the amount and composition of the ash of the *seeds* are much less variable.

In nearly all seeds the largest constituents of the ash are phosphorus pentoxide and potash. In certain seeds generally used in their husk, *e.g.* oats, millet, spelt, and barley, silica is a large constituent.

But in the leaves and stems of plants, phosphorus pentoxide usually forms but a small constituent of the ash, whilst potash and lime become relatively more abundant. In cereals and grasses, silica often forms more than half of the total ash of the straw and chaff.

In addition to the constituents given in the above table, small quantities of oxides of iron and manganese are almost invariably present in vegetable ashes.

Titanium (Wait, J. Amer. Chem. Soc. 1896, 18, 402), aluminium fluorine, and boron (Crampton, Amer. Chem. J. 11, 227, Jay, Compt. rend. 121, 893; Baumert, Ber 21, 3290), are also frequently present in small quantities in the ash of certain plants

Lithium, rubidium, zinc, copper, barium, and arsenic have also been detected in the ash of certain plants grown in soils containing these constituents (Passerini, Chem. Soc. Abstr. 1893, ii. 225; Homberger, *ibid.* 1899, A, ii. 506; Macdougal, *ibid.* 1900, A, ii. 235)

Even chromium, molybdenum, and vanadium have been detected in the ash of fir, oak, vine, and poplar (Demarçay, *ibid.* 1900, 235).

Indeed, the composition of the soil has a great influence upon the amount and composition of the ash of the crop grown upon it, though this influence is much more marked upon the foliage, stem, &c., than upon the seed.

Certain plants, originating from plants of the seashore, *e.g.* asparagus, beet, and carrot, generally leave an ash containing unusually high amounts of chlorine and sodium, and application of common salt as manure to such crops is usually stated to be beneficial, although on no very sufficient evidence

Plants like salt-worts (*Salsola*) and samphire (*Salicornia*) growing on the coast, contain relatively enormous quantities of soda—in the former 6 times, in the latter 14 times, as much soda as of potash.

The ash of the club-moss (*Lycopodium*) contains from 20 to 50 p.c. of alumina.

Manganese is invariably present in tea-leaves, and, according to the writer's observations, is present in the soluble matter (*i.e.* in the infusion).

As already stated, some of the phosphates and sulphates found in the ash of plants result from the oxidation of phosphorus and sulphur organic compounds present in the original plant.

Posternak (Compt. rend. 137, 1903) detected the existence in peas, beans, potatoes, and the seeds of the red fir, pumpkin, white and yellow lupines of *anhydro-oxymethylene diphosphoric acid*—

$$O\begin{cases}CH_2—OPO(OH)_2\\ CH_2—OPO(OH)_2\end{cases}$$

or *inositol phosphoric acid* $C_6H_6(PO_4H_2)_6$. Patton and Hart (Bull. 250 (1904), N. York. Agric. Expt. Station) have shown that about 86 p.c. of the total phosphorus in bran, 81 p.c. in malt sprouts, and 50 p.c. in oats, is soluble in 0·2 p.c. sol. of hydrochloric acid; and that the greater portion of this is present in the bran as calcium, magnesium, and potassium salts of inositol phosphoric acid (*v.* BRAN).

Importance of the Ash Constituents of Foods.

The influence of the mineral matter in the food of animals upon their health and well-being is probably much greater than is generally recognised. Not only is it essential that all the inorganic constituents required for building up the tissues and producing the various digestive and other secretions be supplied in sufficient quantities, but it is important, at least with certain pairs of constituents, that they be supplied in appropriate ratios to each other.

A preponderance of phosphoric acid over lime and magnesia in the diet is probably the cause or a predisposing cause of certain diseases of the bones of horses, mules, and donkeys (Ingle, Jour. Comp. Pathology and Therapeutics, 1907; Jour Agric. Science, 1908, iii. 22; Jour. Roy. Inst. Public Health, 1909); while the ratio of potash to soda in the food has an important bearing upon health, and especially upon the susceptibility to certain diseases, *e.g.* scurvy.

The cereals contain a large excess of phosphoric acid over lime, and the use of an exclusively cereal diet may lead to imperfect bone nutrition (*l.c.*; also Illustrated Poultry Record, 1910).

The necessity of an adequate supply of chlorides in the diet is well recognised, and in many countries the ordinary food supplies of domestic animals have to be supplemented by common salt to ensure healthy existence.

Whenever the rations are restricted to one or two items, there is considerable probability that certain mineral constituents will be lacking or supplied in improper proportions.

It is too often the practice, in discussing the feeding of animals, to devote much consideration to the organic portions of their food, but beyond requiring that sufficient mineral matter or 'bone-forming' material be present, to pay little or no attention to its composition.

Thus bran is widely regarded as a food particularly rich in mineral matter, and therefore valuable for bone nutrition; but the ratio of phosphorus pentoxide to lime in this food is about 11 to 1, and the practice of feeding animals largely upon bran is known to produce a disease of the bones—'bran rachitis' in horses.

Kellner (Scientific Feeding of Animals, 1909) estimates that for oxen, 50 grams of phosphorus pentoxide and 100 grams of lime per 1000 kilos. body weight per day, are required in the food, while for full-grown sheep, 1 gram of the former and 11 grams of lime suffice.

In England, fortunately, hay—either meadow or clover—forms a large part of the rations of farm animals, and this contains a large excess of lime over phosphoric acid, and thus neutralises the opposite preponderance in the grain or cake used with it.

But in South Africa and perhaps some other countries, meadow or clover hay is but little used, and many horses are fed entirely upon oat hay or oat hay and maize. In either case there is a large preponderance of phosphoric acid over lime, and to this fact the prevalence of certain bone diseases is almost certainly due.

Similar considerations apply to other animals kept in confinement, especially to poultry when deprived of a grass run, and to pigs. H.I.

ASIPHYL. *See* ASYPHIL.

ASPARAGINE. *Aminosuccinamic acid* $C_2H_3{\cdot}NH_2(CO_2H)(CO{\cdot}NH_2)$ occurs in two optically active forms, differing in direction of rotatory power and in taste. *Lævo-asparagine*, discovered by Vauquelin and Robiquet (Ann. Chim. anal. 1805, 57, 88) in the young shoots of asparagus (*Asparagus officinalis*, Linn.), is widely distributed in the vegetable kingdom, occurring in most plants at the time of budding and during the flowering period, and, with glutamine, forms the chief non-proteid compounds present in the juice of ripening oranges (Scurti and de Plato, Chem. Zentr. 1908, ii. 16, 1370; Stieger, Zeitsch. physiol. Chem. 1913, 86, 245, 269; Smolenski, Zeitsch. Ver. deut. Zuckerind, 1911, 435; Tutin, Chem. Soc. Trans. 1913, 103, 1274; Chapman, *ibid.* 1914, 105, 1901; Tutin and Clewer, *ibid.* 1914, 570). It is also found in blood (Abderhalden, Zeitsch. physiol. Chem. 1913, 88, 478–483). Miyacha (Bull. Coll. Agric. Imp. Univ. Tokyo, 1897, 2, 458) has shown that in the case of *Pæonia albiflora* and *Thea chinensis*, even old leaves, showing incipient decay, can produce asparagine. It occurs to a larger extent in leguminous plants than in any other natural order, and is most abundant at the time of germination, the quantity being greater in etiolated than in normal plants (Borodin, Bied. Zentr. 1879, 357; *see* also Ritman, Izv. Moskow. Selsk. Khoz. Inst. 18, 212–220; from Abs. Amer. Chem. Soc. 1913, 3144; Nicolaieva, Bull. Agr. Intelligence, 1917, 8, 204). Sachsse (Landsw. Versuchs. Stat. 1874, 17, 88) found that the amount of asparagine in germinating peas increased from 0·67 to 6·94 p.c. during 24 days' growth; and Schulze and Umlauft (*ibid.* 1875, 18, 1) found 17·9 p.c. of asparagine in the dried shoots of *Lupinus luteus* seedlings germinated in the dark in distilled water (*cf.* also Mercadante, Gazz. ital. chim. 1875, 5, 187; Schulze, Landsw. Versuchs. Stat. 1895, 46, 383; Stoklasa, Landw. Jahrb. 1895, 24, 827; Bourquelot and Herissey, J. Pharm. 1898, (vi.) 8, 385; Bréal, Ann. Agron. 1900, 26, 5; Schulze and Barbieri, Landsw. Versuchs. Stat. 21, 63; Kinoshita, Bull. Coll. Agric. Imp. Univ. Tokyo, 1895, 2, 203); Schulze and Bosshard, Zeitsch. physiol. Chem. 1885, 9, 420; Bungener, Bied. Zentr. 1885, 861; Behrens, Bot. Zentr. 1894, 178). Asparagine is one of the decomposition products of proteid matter (Schulze, Bied. Zentr. 1901, 30, 106; Chem. Zentr. 1901, i. 1108; Ber. Deut. Bot. Ges. 1907, 25, 213), and its accumulation in the plant during the periods of germination and budding, particularly when the development occurs in the dark is attributed by Borodin (Bied. Zentr. 1879, 357) and Schulze and Barbieri (J. pr. Chem. 1882, [2] 25, 145), to the absence of carbohydrates which under conditions of normal assimilation effect the reincorporation of amides into proteid molecules; and this view is confirmed by Monteverde (Ann. Agron. 17, 376), who found that branches of lilac plunged in distilled water or 4 p.c. glycerol solution and kept in the dark, contained abundance of asparagine at the end of 15 days, but neither starch nor mannitol. When, however, branches of the same plant were kept in solutions of glucose, sucrose, or mannitol, they formed no asparagine in a month, but contained much mannitol and starch. Another source of asparagine in the plant is its synthetic formation from ammonium salts, urea, or nitrates supplied by the soil. This synthetic production is only possible in the presence of sugar, and under conditions that exclude the formation of proteids (Suzuki, Bull. Coll. Agric. Imp. Univ. Tokyo, 1895, 2, 196). The function of the asparagine in the plant economy is the production of proteid matter; hence the addition of leguminous seeds after steaming to the mash in brewing is recommended by Birner (J. Soc. Chem. Ind. 1882, 333), as the asparagine they yield forms excellent nutriment for the yeast cell; and Kinoshita (Bull. Coll. Agric. Imp. Univ. Tohyo, 1895, 2, 196) found that young shoots of soja bean that showed an increase in asparagine, from 21·5 to 28·7 p.c. after four weeks' natural growth, became poorer in asparagine (18·9–13·7 p.c.) if grown for the same period in methyl alcohol and glycerol solution, but contained reserve proteid matter. According to Ciamician and Ravenna (Atti R. Accad. dei Lincei [5] 20, 1, 614–624), there is an increase of alkaloid in the tobacco plant and date when supplied with asparagine. Morgen, Beger, and Westhausser (Landw. Versachs. Stat. 1911, 75, 265–320), experimenting with sheep, claim that, given a sufficiency of carbohydrate, a deficiency of protein may be made good with ammonium acetate and asparagine.

Asparagine can be extracted from the juice expressed from young vetch seedlings that have germinated in the dark, 10 kilos. of vetch yielding 150 grams of pure asparagine (Piria, Annalen, 1848, 68, 343). Sure and Tottingham found that asparagine is made use of in the nitrogen metabolism of etiolated pea plants (J. Biol. Chem. 1916, 26, 535).

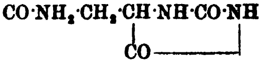
Asparagine crystallises from aqueous solution in large rhombic lævo- hemihedral prisms, $a : b : c :: 0{\cdot}4752 : 1 : 0{\cdot}8294$ (Freundler, Compt. rend. 1897, 125, 657), containing $1H_2O$, which it loses at 100°, and then melts at 234°–235° (Michael, Ber. 1895, 28, 1620); it has a sp.gr. 1·5434 at 14·8°/4° (Piutti, Gazz. chim. ital. 1904, 34, 36); the molecular heat of combustion is 448·4 Cals., and the heat of formation 205·1 Cals. (Berthelot and Andre, Compt. rend. 1890, 120, 884; *see* also Emery and Benedict, Amer. J. Physiol. 28, 301–307); it is sparingly soluble in cold, readily so in hot water—1 part dissolves in 82 parts of water at 10°, in 47 parts at 20° (Becker, Ber. 1881, 14, 1028), in 58 parts at 13°, and 1·89 parts at 100° (Guareschi, Gazz. chim. ital. 1876, 6, 370; *cf.* Bresler, Zeitsch. physikal. Chem. 1904, 47, 611). The aqueous solution is weakly acid, has an insipid and disagreeable taste, and is lævo-rotatory $[a]_D -5° 4'$ (Piutti, Compt. rend. 1886, 103, 134); the rotatory power of the solution is increased by raising the temperature and by the addition of alkalis, inverted by mineral acids and by solutions of certain inorganic salts and destroyed by acetic acid (Champion and Pellet, Compt.

rend. 1876, 82, 819; Becker, Ber. 1881, 14, 1028; Smolenski, Zeitsch. Ver. deut. Zuckerind, 1910, 215; and 1912, 791; Pellet, Zeitsch. Ver. deut. Zuckerind, 1911, 435–443; Clough, Chem. Soc. Trans. 1915, 107, 1513; Andrlik and Stanek, Zeitsch. Zuckerind. Böhm. 31, 417). Advantage is taken of this last fact to eliminate the error due to the presence of asparagine in saccharimetric determinations of sugar liquors from beets and canes. Asparagine is partially hydrolysed by boiling with water, forming *aspartic acid* (*aminosuccinic acid*) $C_2H_3{\cdot}NH_2(CO_2H)_2$ and ammonia; the change is rapid and complete when excess of barium hydroxide or dilute hydrochloric or sulphuric acid is employed (Schulze, Landsw. Versuchs. Stat. 29, 233); by the action of potassium permanganate, asparagine is oxidised to carbamide and ammonia; and when used in 5 p.c. aqueous solution for the culture of *Bacillus pyrocyanicus*, it is converted into aspartic acid after 60 hours, and completely decomposed after 72 hours (Arnaud and Charrin, Compt. rend. 1891, 112, 755; Adeney, Proc. Roy. Irish Acad. 1905, 25, 6). An aqueous solution in presence of sunlight yields acetaldehyde, ammonia, and carbon dioxide (Ganassini, Giorn. Farm. Chim. 1912, 62, 439–444). Under the action of enzymes, asparagine yields a mixture of formic, propionic, and succinic acids (Neuberg and Cappezzuoli, Biochem. Zeitsch. 1909, 18, 424), and a similar change is effected by brewer's yeast (Effront, Mon. Sci. 1909, (iv.) 23, i. 145; and Kurono, J. Agric. Tokyo, 1911, 1, 295–330).

The presence of asparagine (1 : 19,000) may be detected by means of triketohydrindene hydrate (Abderhalden and Schmidt, Zeitsch. physiol. Chem. 85, 143–147).

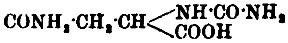
The estimation of asparagine is based upon its quantitative conversion into aspartic acid and ammonia by the action of hydrochloric acid, the aspartic acid may be removed in the form of its sparingly soluble copper salt (Engel, Compt. rend. 1888, 106, 1734) and the ammonia determined by Sachsse's method (J. pr. Chem. 1872, [2] 6, 118) or by one of the modifications of Schloessing's method described by Meunier (Ann. Agron. 6, 275), by Schulze (J. pr. Chem. 1885, [2] 31, 233), or by Brown and Millar (J. Soc. Chem. Ind. 1904, 135). Palet (Anal. Soc. Quim. Argentina, 1917, 5, 95) points out that the results of the estimation by Schloessing's method are influenced by the employment of different alkalis.

Asparagine has feeble basic and acidic properties, and forms salts with acids and bases (Chautard and Dessaigne, Annalen, 1848, 68, 349; Dessaigne, Annalen, 1852, 82, 237; Smolka, Monatsh. 1887, 6, 915); it also forms double compounds with certain salts of the heavy metals, the sparing solubility of the compound with mercuric nitrate is made use of in isolating small quantities of asparagine from solutions containing carbohydrates (Schulze, Ber. 1882, 15, 2855); it forms stable complex internal salts with certain heavy metals; the chromium salt $Cr(C_4H_7O_3N_2)_3$ crystallises in microscopic rose-violet needles (Tschugaeff, Serbin, Compt. rend. 1910, 151, 1361–1363) and combines with copper hydroxide to yield a copper complex of the formula $Cu(C_4H_7O_3N_2)_2$ (Kober and Sugiura, J. Biol. Chem. 1912–1913, 13, 1–13); the *alum* $(C_4H_8O_3N_2)_2H_2SO_4,Al_2(SO_4)_3,24H_2O$ forms octahedral crystals. Asparagine is converted into *l*-chlorosuccinic acid and fumaric acid by the action of nitrosyl chloride in hydrochloric acid solution (Tilden and Forster, Chem. Soc. Trans. 1895, 67, 489); it yields the amide of uramidosuccinic anhydride



$$\begin{array}{l}CO{\cdot}NH_2{\cdot}CH_2{\cdot}CH{\cdot}NH{\cdot}CO{\cdot}NH\\ \qquad\qquad\qquad\quad\ \ |\qquad\qquad\quad\ \ |\\ \qquad\qquad\qquad\quad CO\text{———————}\!\rfloor\end{array}$$

when fused with carbamide (Guareschi, Gazz. chim. ital. 1876, 6, 370), and is converted into amidosuccinuric acid



$$CONH_2{\cdot}CH_2{\cdot}CH\begin{array}{l}\diagup NH{\cdot}CO{\cdot}NH_2\\ \diagdown COOH\end{array}$$

m.p. 137°–138°, by the action of potassium cyanate (Guareschi, Ber. 1877, 10, 1747). Certain condensation products of asparagine with other amino- acids are described by Fischer (Ber. 1904, 37, 4585; 1907, 40, 2048), *chloroacetylasparagine*, m.p. 148°–149° (corr.); *glycylasparagine*, m.p. 216°, $[\alpha]_D -6{\cdot}4°$ at 20°; *anhydroglycylasparagine*, decomposing at 274°; d-*leucyl*-l-*asparagine*, decomposing at 230° (corr.), $[\alpha]_D -53{\cdot}6°$ at 20°; l-*leucyl*-d-*asparagine*, m.p. 228° (corr.), $[\alpha]_D +17{\cdot}8°$; *asparagylaspartic acid*, decomposing at 120°. Sasaki (Beitr. Chem. Physiol. Path. 1907, 10, 120) describes a *benzoylpolypeptide* of asparagine $C_{19}H_{24}O_8N_6$, decomposing at 210°, and giving the biuret reaction.

Benzyl hydrogen asparaginedithiocarboxylate

$$CO_2H\ C_2H_3(CONH_2){\cdot}NH{\cdot}CS_2{\cdot}CH_2Ph$$

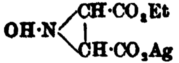
has m.p. 180°. The barium salt crystallises in slender needles (Siegfried and Weidenhaupt, Zeitsch. physiol. Chem. 1910, 70, 152–160).

As regards the alimentary value of asparagine, it has been found that in the case of herbivorous mammals and geese, asparagine has a proteid-sparing action, and under appropriate conditions prevents waste and causes the formation of proteid matter (Weiske, Bied. Zentr. 1879, 744; 1882, 312; Zeit. für. Biol. 15, 261; 20, 276; Landws. Versuchs. Stat. 1888, 34, 303; Rosenfeld, Zeitsch. Ver. deut. Zuckerind 1900, [539] 1055, from. J. Soc. Chem. Ind. 1901, 271). According to Zuntz and Muller (Pflüger's Archiv. 1906, 112, 245), the proteid-sparing action of asparagine is the result of a kind of symbiosis, the bacteria in the paunch of the ruminants decomposing the asparagine in preference to the protein in the food. In the case of omnivora and carnivora, asparagine exerts only a diuretic action (Murok and Voit, Bied. Zentr. 1884, 749; Politis, Zeit. Biol. 1893, 27, 492; Mauthner, *ibid.* 507; Gabriel and Voit, *ibid.* 29, 115, 125; Levena and Kohn, Amer. Jour. Physiol. 1909, 23, 324; *see*, however, Abderhalden, Zeitsch. physiol. Chem. 1911, 74, 481–504; and Nitsche, Beitr. Phys. 1914, 1, 53–89).

Dextro-asparagine was discovered by Piutti (Ber. 1886, 19, 1691) in the young shoots of the vetch (*Vicia sativa*, Linn.) 6500 kilos. of vetch buds yielded 20 kilos. of crude asparagine, from which 100 grams of pure dextro-asparagine was isolated; it is slightly more soluble than the lævo- compound; the solution has an intensely sweet taste, is dextro-rotatory in neutral or alkaline solution $[\alpha]_D + 5{\cdot}41°$ (Piutti, Compt. rend. 1886, 103, 134), and lævo-rotatory in acid solution; it forms large rhombic dextrohemihedral crystals, $a : b : c :: 0{\cdot}4741 : 1 : 0{\cdot}8310$ (Freundler, Compt. rend. 1897, 125, 657). A solution of equal parts of the two optically active asparagines is optically inactive, but the two varieties separate on crystallisation, twinning frequently taking place between the left and right crystals (Piutti, Compt. rend. 1886, 103, 134). *d*- and *l*-Asparagine can be separated by fractional crystallisation from hot water although both have the same solubility at 20°. The solubility of *l*-asparagine, previously heated, is at least doubled after cooling, and only slowly returns to its original value (Erlenmeyer, Biochem. Zeitsch. 52, 439–470). The silver salt of *dl-asparagine* $C_4H_7O_3N_2Ag$, forms wart-like clusters of crystals, m.p. 182°–183° (decomposed) (Abderhalden and Kautzsch, Zeitsch. physiol. Chem. 1912, 78, 115–127).

According to Pringsheim (Zeitsch. physiol. Chem. 1910, 65, 89), the *d*-asparagine found by Piutti in the mother liquors from which the *l*-asparagine had been isolated, was formed by the racemisation of the *l*-asparagine during the process of evaporation of the solutions. The author states that after boiling *l*-asparagine [$[\alpha]_D^{20°} + 36{\cdot}19°$, in $N/10$ hydrochloric acid solution] for 12 hours, with water, and subsequent fractional crystallisation, he obtained a fraction that had $[\alpha]_D^{20°} - 15{\cdot}3°$ in $N/10$ hydrochloric acid solution, and therefore contained *d*-asparagine.

In addition to the two asparagines already described, there is a third form known as *α*-asparagine; it does not occur naturally; is optically inactive, crystallises in the triclinic system, $a : b : c = 1{\cdot}5957 : 1 : 0{\cdot}5668$; $\alpha = 91°19'$; $\beta = 113°/12'$, $\gamma = 83°\ 48'$ (Brugnatelli); and has a sp.gr. 1·454 at 14·8°/4° (Piutti, Gazz. chim. ital. 1904, 34, ii. 36), and is not structurally identical with the optically active or *β*-asparagines. The three asparagines have been synthesised by Piutti (Gazz. chim. ital. 1887, 17, 126; 1888, 18, 457) by the following methods, that leave no doubt as to the constitution of the compounds. By the reduction of the oxime of oxalacetic ester $CO_2Et{\cdot}CH_2{\cdot}C(NOH){\cdot}CO_2Et$ with sodium amalgam and partial saponification of the product, Piutti obtained two different ethyl hydrogen aspartates, melting at 165° and 200° respectively. The ester melting at 165° is identical with the compound obtained by reducing Ebert's (Annalen, 1885, 229, 45) monoethyl ester of oximinosuccinic acid, which has the formula $CO_2H{\cdot}CH_2{\cdot}C(NOH){\cdot}CO_2Et$, since on heating it loses CO_2 and forms oximinopropionic ester $CH_3{\cdot}C(NOH){\cdot}CO_2Et$. It follows, therefore, that the ethyl hydrogen aspartate melting at 165° is the monoethyl *α*-aspartate $CO_2H{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2Et$, and the ester melting at 200° must be the monoethyl *β*-aspartate $CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO_2Et$. When these esters are treated with alcoholic ammonia, they are converted into the corresponding asparagines; the ester m.p. 165° gives inactive *α-asparagine* $CO_2H{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CONH_2$, and the ester m.p. 200° yields a mixture of *d*- and *l*- *β*-asparagines $CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CONH_2$. From silver ethyl *γ*-oximinosuccinate



$$\mathrm{OH{\cdot}N}\left\langle\begin{array}{l}\mathrm{CH{\cdot}CO_2Et}\\ \ |\\ \mathrm{CH{\cdot}CO_2Ag}\end{array}\right.$$

Piutti (Gazz. chim. ital. 1890, 20, 402) obtained a mixture of the three asparagines, the *α*-asparagine readily gave up its water of crystallisation in a vacuum, and fell to powder; and the *d*- and *l*- *β*-asparagines could then be separated by hand sorting. A mixture of the three asparagines was also obtained by the action of alcoholic ammonia on the ethyl hydrogen ester of inactive aspartic acid (Piutti, Gazz. ital. chim. 1887, 17, 126; 1888, 18, 457). Körner and Menozzi (Gazz. ital. chim. 1887, 17, 171, 226) effected the synthesis of the *d*- and *l*- *β*-asparagines from ethyl bromosuccinate, from ethyl fumarate or ethyl maleate, by the action of alcoholic ammonia; and similar results were obtained by Piutti (Ber. 1896, 29, 2069) with *l*-bromosuccinamic acid or maleic anhydride.

β-Ethylasparagine $CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO{\cdot}NHEt$, m.p. 258°–260°, with decomposition, and *β-allylasparagine* $CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_3H_5$, melting and decomposing at 258°–261°, prepared by the action of the corresponding alkylamine on *β*-ethylaspartic acid, yield optically inactive solutions (Piutti, Gazz. chim. ital. 1888, 18, 478). M. A. W.

ASPARAGUS. The shoots of this plant (*Asparagus officinalis*) are used as a table vegetable.

	Water	Protein	Fat	Carbo-hydrates	Ash
Average composition	94·0	1·8	0·2	3·3	0·7

The nitrogenous matter of asparagus consists largely of *amino-succinamic acid* $CO(NH_2){\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$, a substance known (from its discovery, in 1805, in asparagus shoots) as *asparagine* (*q.v.*).

Coniferin and vanillin have also been found in the sap and cellular tissue (Lippmann, Ber. 1886, 18, 3355); Tanret (Compt. rend. 1909, 149, 48) describes two new carbohydrates as occurring in approximately equal quantities in asparagus roots—*asparagose* $(C_6H_{10}O_5)_n{\cdot}H_2O$, where $n = 15$ or 16, crystallising in microscopic needles, soluble in water, insoluble in absolute alcohol, m.p. 198°–200°, gives no colouration with iodine, and does not reduce Fehling's solution; and *ψ-asparagose*, a white, hygroscopic substance more soluble than asparagose. Both substances are hydrolysed by invertase, yielding dextrose and lævulose.

The seeds of asparagus were examined by Peters (Arch. Pharm. 1902, 240, 53), and were found to contain water 11·5, woody fibre 8·2, nitrogen 3·0, and oil 15·3 p.c. Starch was not present, but a reserve cellulose (mannan), capable of yielding *d*-mannose on boiling with dilute hydrochloric acid, occurred; 37·5 p.c. of the weight of the seeds, of mannose was obtained. The oil was reddish yellow, had a sp.gr. of 0·928 at 15°, and an iodine number of 137·1. H. I.

ASPARTIC ACID. *Aminosuccinic acid* $CO_2H{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$, found in young sugar cane and in molasses of sugar beet (Scheibler, J. 1886, 399), in young shoots of the gourd (Schulze and Barbieri, Ber. 1878, 11, 710), and in mulberry leaves (Mimuroto, J. Agric. Tokyo, 1912, 5, 63–65), has been observed in diseased liver (Taylor, Zeitsch. physiol. Chem. 1901, 34, 580), and occurs in certain glands of *Tritonium nodosum*, the posterior portion of the gland when stimulated secretes an acid fluid from which aspartic acid immediately crystallises. As aspartic acid is soluble in sea-water, it is probably employed by the animal in destroying the calcareous shells of the other shellfish that form its food (Henze, Ber. 1901, 34, 348).

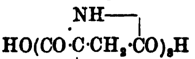
Aspartic acid is prepared by hydrolysing asparagine by means of hydrochloric or sulphuric acid, lime, baryta, lead oxide or potash (Plisson, Ann. Chim. Phys. [2] 35, 175; 37, 81; 40, 303; Schulze, Landsw. Versuchs. Stat. 29, 233); it is one of the degradation products of proteid matter, and is obtained when casein or proteid is heated with (1) dilute sulphuric acid (Kreussler, J. pr. Chem. 1869, 107, 239; Ritthausen, *ibid.* 218; Fischer, Zeitsch. physiol. Chem. 1901, 33, 151; 1902, 35, 70; 36, 462); (2) bromine or with stannous chloride (Hlasiwetz and Habermann, Annalen, 1871, 159, 325; 1873, 169, 162). Aspartic acid is produced by the oxidation of conglutin with potassium permanganate (Pott, J. pr. Chem. 1873, [2] 6, 91), by the pancreatic digestion of fresh blood fibrin at 40°–50° (Radziejewski and Salkowski, Ber. 1874, 7, 1050), or of gluten (Knieriem, Zeitsch. f. Biol. 1876, 11, 198); and is one of the acid constituents of Kühne's 'antipeptone' (Kutscher, Zeitsch. physiol. Chem. 1898, 25, 195; 26, 110).

The naturally occurring aspartic acid is lævo-rotatory and the same *l-aspartic acid* is obtained by hydrolysis of *lævo*-asparagine (Schiff, Ber. 1884, 17, 2929); it crystallises in rhombic prisms, m.p. 270°–271° (Michael, Ber. 1895, 28, 1629), is sparingly soluble in water, 100 grams of water dissolve y mg. of the acid at t°, where

$$y=372+14{\cdot}1t-0{\cdot}18124t^2+0{\cdot}0053t^3$$

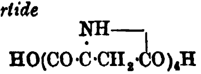
(Engel, Compt. rend. 1888, 106, 1734). A solution containing 1·873 p.c. of acid is feebly dextro-rotatory below 75°, but lævo-rotatory above that temperature; $[\alpha]_D 5{\cdot}87°$ (Wood, Chem. Soc. Trans. 1914, 105, 1992); in alkaline solutions the substance is strongly lævo-, and in acids strongly dextro-, rotatory, and dextrorotatory in aqueous solutions of certain inorganic salts (Becker, Ber. 1881, 14, 1028). The rotatory power in acid and alkali reaches a maximum value under definite conditions of concentration (Wood, *ibid.* 1914, 105, 1992; Clough, Chem. Soc. Trans. 1915, 107, 1510). The heat of combustion is 387·2 Cals., the heat of formation 231·9 Cals. (Berthelot and André, Compt. rend. 1890, 110, 884); the heat of dissolution at 16° is −7·25 Cals., heat of neutralisation by sodium hydroxide +3·0 Cals. for the first, and +3·5 Cals. for the second equivalent (Berthelot, Compt. rend. 1891, 112, 829). Aspartic acid is readily soluble in aqueous solutions of certain mineral salts; for this reason Schiff (Ber. 1886, 17, 2929) recommends that in its preparation from asparagine by boiling with hydrochloric acid, the minimum quantity (2 mols.) of acid be employed, and the excess afterwards neutralised by ammonia (1 mol.); by adopting this precaution, a yield of 90 p.c. of the theoretical is obtained. For the estimation of aspartic acid in the hydrolysis products of proteid, *see* Foreman (Bio-Chem. J. 1914, 8, 463).

Aspartic acid forms salts with acid and bases, the copper salt $C_4H_5O_4NCu,4\frac{1}{2}H_2O$ or $C_4H_5O_4NCu,5H_2O$, forms pale-blue needles almost insoluble in cold water (Engel, *l.c.*; Abderhalden and Weil, Zeitsch. physiol. Chem. 1911, 72, 23). The calcium salt can be precipitated quantitatively by means of alcohol (Foreman, *ibid.* 471). The mono-silver salt melts 216°–217° with decomposition (Abderhalden and Kautzsch, Zeitsch. physiol. Chem. 1912, 78, 123). A uranyl salt $UO_2(C_4H_5O_4N)_2,3H_2O$ is formed by double decomposition (Mazzucchelli and D'Alceo, Atti. R. Accad. Lincei, 1912, [5] 2, 11, 620–626). Aspartic hydrochloride $C_4H_7O_4N{\cdot}HCl$, softens with gas evolution at 178°, and then does not alter up to 280° (Philippi and Uhl, Monatsh. 34, 717–731). Aspartic acid is oxidised by hydrogen peroxide to the semi-aldehyde of malonic acid which breaks up into acetaldehyde and carbon dioxide (Dakin, J. Biol. Chem. 1909, 5, 409); it is capable of furnishing the nitrogen required for the development of *B-coli communis* in presence of mannitol and glucose, becoming reduced to ammonium succinate (Harden, Chem. Soc. Trans. 1901, 623), and by enzyme action it is decomposed into formic, propionic, and succinic acids (Neuberg and Cappezzuoli, Biochem. Zeitsch. 1909, 18, 424; Borchardt, Zeitsch. physiol. Chem. 1909, 59, 96; Abderhalden and Fodor, Zeitsch. physiol. Chem. 1913, 85, 119, 130). On heating it with glucose under pressure Bauer and Barshall obtained succinic acid, and suggest that aspartic acid is the source of the succinic acid found in meat extract (Chem. Zentr. 1911, 2, 1367). When aspartic acid is heated at 190°–200° for 20 hours, and the product boiled with water, two sparingly soluble anhydrides, *octoaspartide*



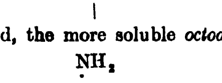
$$\mathrm{HO(CO\cdot\underset{|}{\overset{\overset{NH—}{\cdot}}{C}}\cdot CH_2\cdot CO)_8H}$$

and *tetraspartide*



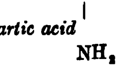
$$\mathrm{HO(CO\cdot\underset{|}{\overset{\overset{NH—}{\cdot}}{C}}\cdot CH_2\cdot CO)_4H}$$

are obtained, the more soluble *octoaspartic*



$$\mathrm{HO(CO\cdot\underset{|}{\overset{\overset{NH_2}{\cdot}}{C}}\cdot CH_2\cdot CO_2H)_8H}$$

and *tetraspartic acid*



$$\mathrm{HO(CO\cdot\underset{|}{\overset{\overset{NH_2}{\cdot}}{C}}\cdot CH_2\cdot CO_2H)_4H}$$

can be isolated from the filtrate (Schiff, Ber. 1897, 30, 2449). Dimethyl or diethyl sulphate and *l*-aspartic acid in alkaline solution give fumaric acid and alkylated ammonia derivatives (Novák, Ber. 1912, 45, 834–850). The following alkyl esters of aspartic acid are described: *Monoethyl asparate hydrochloride*, m.p. 199°; *diethyl* and *dimethyl aspartate hydrochlorides*, deliquescent solids (Curtius and Koch, Ber. 1885, 18, 1293; Wegscheiden and Frankl, Monatsh. 1906, 27, 487), *ethyl β-aspartate* $CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO_2Et$, m.p. 200°; *ethyl α-aspartate* $CO_2H{\cdot}CH_2{\cdot}CH(NH_2)CO_2Et$, m.p. 165° (Piutti, Chem. Zentr. 1888, 1459). The methyl, ethyl, allyl, propyl, *iso*propyl, butyl, *iso*butyl, and *iso*amyl hydrogen esters are dextro-rotatory at ordinary and lævo-rotatory at higher temperatures, and form sparingly soluble copper salts (Piutti and Maghi, Gazz. chim. ital. 1906, 36, ii. 738). *l*-Diethylaspartate has b.p. 126·5°/11 mm. pressure; sp.gr. 1·089 at 17° and $[\alpha]_D^{20°} = -9·46°$ (Fischer, Sitzungber, Akad. Wiss. Berlin, 1900, 48, 1062), or b.p. 126°–127°/10 mm., 150°–152°/25 mm. pressure, and forms a yellow *picrolonate* $C_8H_{15}O_4N,C_{10}H_8O_5N_4$, m.p. 290° (Schmidt and Widman, Ber. 1909, 42, 497). Aspartic acid and ethyl metaphosphate yield a derivative of the composition $C_8H_{12}O_7NP$ (Langheld, Ber. 1911, 44, 2076–2086).

Of the *acyl* derivatives of aspartic acid, the *benzenesulphonyl* derivative $SO_2Ph·NH·C_2H_3(CO_2H)_2$ melts at 170° (Hedin, Ber. 1891, 23, 3196); the *hippuryl* derivative $NHBz·CH_2·CO·NH·C_2H_3(CO_2H)_2$, m.p. 191° (Curtius and Curtius, J. pr. Chem. 1904, (ii.) 70, 158); *benzoyl l-aspartic acid*, m.p. 184°–185° (corr.); has $[\alpha]_D^{20°} + 37·4°$, *leucyl aspartic acid* $CH_2Pr^\beta·CH(NH_2)·CO·NH·C_2H_3(CO_2H)_2,H_2O$ decomposes at 180°–182° (corr.) (Fischer and Koenigs, Ber. 1904, 37, 4585); and the *picryl* derivative $C_{10}H_8O_{10}N_4$ has m.p. 137°; *diethylchloracetyl aspartate*

$$COOEt·CH_2·CH·NH(CO·CH_2Cl)COOEt$$

(Fischer and Koenigs, Ber. 1904, 37, 4585; Bornwater, Rec. trav. chim. 1917, 36, 281) has m.p. 46°–47°; k.p. 139°; *aspartic diamide* $C_2H_3(NH_2)(CONH_2)_2$, m.p. 131°, has $[\alpha]_D - 7°$, and gives the biuret reaction (Fischer and Koenigs, *l.c.*). Aspartic acid resembles asparagine in its physiological action (Salkowski, Zeitsch. physiol. Chem. 1904, 42, 1207; Andrlík and Velich, Zeitsch. Zuckerind. Böhm, 1908, 32, 313).

d-Aspartic acid, obtained by hydrolysis of *d*-asparagine (Piutti, Ber. 1886, 19, 1694), or from *l*-bromosuccinic acid and aqueous ammonia at −40°, a Walden rearrangement taking place (Fischer and Raske, Ber. 1907, 40, 1051); is also obtained from a solution of the racemic acid [(*d*+*l*) aspartic acid] which has been innoculated with a mould grown on *l*-aspartic acid (Engel, Compt. rend. 1887, 106, 1734). *Benzoyl d-aspartic acid*, obtained by Fischer (Ber. 1899, 32, 2451), by the resolution of the racemic compound, through the brucine salts, has m.p. 181°–182°, $[\alpha]_D^{20°} - 37·6°$ in alkaline solution.

Inactive, *(d+l)-aspartic acid*, prepared by the action of boiling hydrochloric or nitric acid on the product obtained by heating the ammonium salts of malic, maleïc, or fumaric acids (Dessaigne, Compt. rend. 1850, 30, 324); by heating an aqueous solution of the hydrochloride of *l*-aspartic acid at 170°–180° for some hours (Michael and Wing, Ber. 1884, [1] 2984); by heating *d*- or *l*-aspartic acid with 2 mols. HCl (sp.gr. 1·107) at 170°–180°, or from an aqueous solution of equal parts of the *d*- and *l*- acids; the racemic acid crystallises out (Piutti, Ber. 1886, 19, 1694); by reducing and hydrolysing the sodium salt of ethyl oximino-oxalacetate (Piutti, Chem. Zentr. 1888, 68). (*d*+*l*)-Aspartic acid forms small monoclinic prisms; 100 grams of water dissolve *y* mg. of the acid at *t*°, where

$$y = 517 + 21·693t - 0·165t^2 + 0·0079t^3$$

(Engel, Compt. rend. 1888, 106, 1734). The copper salt $CuC_4H_5O_4N,4\frac{1}{2}H_2O$ is dark-blue (Engel, *l.c.*). *dl-Aspartic acid picrolonate* forms long slender crystals with square ends decomposing at 130° (Levene and Slyke, Bio-Chem. J. 1912, 12, 127–139). The *benzoyl* derivative has m.p. 164°–165° (corr.), and can be resolved into its active components by crystallising the brucine salt (Fischer, Ber. 1899, 32, 2451).

M. A. W.

ASPHALT. *Compact bitumen*, *Mineral pitch*, *Jews' pitch*, *Bitumen of Judæa.* (*Judenpech*, *Erdpech*, *Bergpech*, Ger.; *Goudron minéral*, Fr.) A name given to the solid varieties of bitumen. In its purest form asphalt presents the appearance of a black or brownish-black solid substance, possessing a bright conchoidal fracture. It melts at 100°, burning with a brilliant flame and emitting a bituminous odour. Sp.gr. 1·0–1·68. Asphalt is insoluble in alcohol and water, soluble in about five times its weight of naphtha, and in benzol. It is dissolved by alkalis and alkaline carbonates.

By dry distillation a yellow oil, Asphalt oil, is obtained. It consists of hydrocarbons mixed with a small quantity of oxidised matter. It begins to boil at 90°, but the boiling-point gradually rises to 250°. The portion boiling below 200° has the sp.gr. 0·817 at 15°; that above 200° has a sp.gr. of 0·868 at 15°. Both portions gave by analysis about 87·5 p.c. carbon, 11·6 p.c. hydrogen, and 0·9 p.c. oxygen, which is nearly the composition of oil of amber (Völckel, Annalen, 88, 139). Nitric acid converts it into a resin, having the odour of musk and the taste of bitter almonds.

Boussingault obtained from the asphalt of Bechelbrunn a pale-yellow oil, *petrolene*, having a faint taste and bituminous odour, of sp.gr. 0·891 at 21°, and boiling at 280°.

By heating asphalt to 250° for 48 hours, the volatile oils are driven off; a black solid substance, *asphaltene*, is obtained. It becomes soft and elastic about 300°.

The purest asphalt is found on the shores of the Dead Sea and in the pitch lakes of Trinidad and Mexico. Rocks more or less impregnated with bitumen, to which the name earthy or crude asphalt is given, are found at the Poldice mines, Cornwall; near Matlock, Derbyshire; at Haughmond Hill, Shropshire; at the Hotwells, near Bristol; in the limestone near Glasgow; the freestone near Edinburgh; and generally throughout the Orkneys. Large deposits occur also at Seyssel, Dépt. de l'Ain; at Bechelbrunn and Lobsann, Lower Rhine; at Bastennes and Dax, in the Dépt. des Landes; in the Val de Travers, Neuchatel, in Kentucky, and other places.

Asphalt is separated from the minerals with which it is associated either by melting the mass, allowing the earthy matters to subside and removing the bitumen; or by boiling with water, which causes the bitumen to run out in the melted state; or by the action of hydrochloric acid, which dissolves the calcium carbonate and leaves the asphalt; or with oil of turpentine, which dissolves out the bitumen. Murrie (J. Soc. Chem. Ind. 3, 182) describes the methods used in Italy for the extraction of bitumen from crude asphalt.

The Val de Travers asphalt contains about 20 p.c. of bitumen, and it only requires the addition of 6 to 8 p.c. of mineral or coal tar to convert it into a plastic, workable mastic of good quality for pavements and hydraulic works.

The modern method of laying down asphalt pavement is to first prepare a foundation of concrete the surface of which is carefully flattened. On this even surface, when thoroughly dry, the melted asphalt is spread with a wooden trowel, and the surface is finally smoothed over. The liquid Val de Travers, Limmer's, and Barnett's asphalts used for this purpose are all mixed with grit or sand, and so present rougher surfaces than those pavings which consist of asphalt alone. Brande (D. R. P. 4993, 1878) mixes ground slag with the asphalt instead of sand.

Another method of paving is to break up the bituminous ore, and heat the fragments till they crumble to powder. A layer of this hot powder, from 16 to 20 inches thick, is laid on the dry concrete and compressed by stamping with hot irons.

Artificial asphalt, or gas-tar asphalt, is a mixture of chalk, sand, or limestone with the thick, pitchy residue obtained by evaporating the more volatile portions of gas tar. The mineral substance must be heated to expel moisture and adhering air, and then added to the strongly heated pitch.

In addition to the use of asphalt for pavements, water-tight tanks, and coatings for iron tubes used for conveying gas or water, &c., it is used in photography, in photo-lithography, and photo-engraving, owing to the asphalt becoming insoluble in turpentine after exposure to light. In the latter case copper plates are covered with a thin coating of pure asphaltum, or bitumen of Judæa, dissolved in benzene or chloroform. When dry, the plate is exposed behind a film to bright sunlight for half an hour, and then developed by first softening the soluble portion of the asphaltum with olive oil, to which subsequently a little turpentine is added. As soon as the lines are bare the turpentine and oil must be washed away by the action of water.

For the preparation of American supplies of asphalt from petroleum, *see* Day (Min. and Eng. World, 1913; J. Soc. Chem. Ind. 1913, 32, 1057).

Methods for preparing asphalt for paving and other purposes are described by Dagusan (D. R. P. 4999, 1878; Dingl. poly. J. 232, 547); Kalilbetzer (D. R. P. 5646, 1878); Zadig and Neuberg (D. R. P. 5678, 1878; Dingl. poly. J. 233, 490); Clark (Eng. Pat. 8036, 1884; J. Soc. Chem. Ind. 5, 183); Kettmann (Eng. Pat. 12425, 1884; J. Soc. Chem. Ind. 4, 675); Richter (Siefenseid Zeit. 23, 272; J. Soc. Chem. Ind. 2, 474).

On the effect of sulphur in producing hard bitumen, *see* Brooks and Humphrey (J. Soc. Chem. Ind. 1917, 997). On the effect of exposure to air on different bitumens, *see* Reeve and Lewis (*idem*. 998).

Native asphalt can be distinguished from artificial asphalt by extracting with carbon disulphide, filtering, evaporating to dryness, and heating the residue till it can be ground to a fine powder; 0·1 gram is treated with 5 c.c. of fuming sulphuric acid for 24 hours, and is then mixed, with continuous stirring, with 10 c.c. of water. If pitch or coal tar be present, the solution will be of a dark-brown or blackish tint; if not, the solution will be of a light-yellow colour (*v.* PITCH).

For the detection of petroleum- or coal-tar pitch in natural asphalt, *see* Marcusson (Chem. Rev. Fett u. Harz-Ind. 1911, 18, 47; J. Soc. Chem. Ind. 1911, 30, 480; Zeitsch. angew. Chem. 1913, 26, 91; J. Soc. Chem. Ind. 1913, 32, 223); Pailler (J. Ind. Eng. Chem. 1914, 6, 286); Loebell (Chem. Zeit. 1914, 18; Marcusson, *ibid.* 1914, 38, 813, 822).

ASPHODEL. The tuberous roots of *Asphodèle de Sardaigne*, of *Asphodelus ramosus* (Linn.), and other species of the same genus, contain a fermentable substance from which alcohol may be prepared (*cf.* Rivière and Bailhache, Compt. rend. 1895, 121, 659). By drying and coarsely grinding the tubers, Landerer obtained a powder which, mixed with water, formed a strong glue. Badoil and Lienders obtain tannin from the pulp left after the extraction of the alcohol.

ASPIDIN, ASPIDINOL *v.* FILIX-MAS.

ASPIDOSAMINE, ASPIDOSPERMATINE, and **ASPIDOSPERMINE** *v.* QUEBRACHO ALKALOIDS.

ASPIRATORS. Aspirators are used to draw air or other gases through any apparatus connected with them, and were probably first employed by Brunner in his analyses of air, 1830–1840 (Pogg. Ann. 20, 274; 24, 569; 31, 1). The process of aspiration or inhaling of air is, however, most common, being necessary to the life of animals and to the ventilation of buildings, mines, &c., to change the air so that it may support life. In other analyses of air by Dumas and Boussingault, an exhausted globe or jar was used as an aspirator (1841, Ann. Chim. Phys. [3] iii. 257). When a vessel is emptied of liquid, air must enter to take its place, and the common aspirator, in its various forms, is a vessel with two openings, the lower to serve as outlet for the water or liquid, and the upper as inlet for the air or gas to be aspirated. With suitable fittings a siphon may be used instead of the lower opening, or the apparatus may be modified into a bell-jar standing over a basin or large jar, the air being drawn in through the neck of the bell-jar. This is Mohr's aspirator, which is sometimes poised like a gasholder to facilitate filling and emptying of the bell-jar (Mohr, Lehrbuch der Titrirmethode, 1855, Brunswick).

From their introduction, aspirators were used not only to draw in gases through apparatus and reagents employed, at a regulated rate, but also to measure the gases so manipulated by simply measuring or weighing the liquid run out of the aspirator. For approximate readings aspirators of glass may be graduated, and those of metal may be provided with gauge glasses.

Numerous forms of the simple aspirator have been invented by Brunner, Regnault, Mohr, and others. Fig. 1 is perhaps the form in most frequent use, and is generally of glass, plain or graduated. Fig. 2 is a very convenient form, described by Clemens Winkler (Industrie-Gase, 1877, 39-41) constructed of zinc plate and supported on a wooden tripod. The second tap below, on the side tube, is useful in filling the aspirator with water. Fig. 3 is the form often used in testing the gases from chemical works. It is simply a cubical or rectangular box made of sheet lead, with a graduated gauge glass, and can be opened at A to fill it with water.

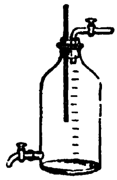


FIG. 1.

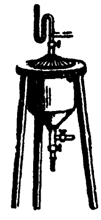


FIG. 2.

Double aspirators. In short operations the simple aspirator requires no refilling nor special attention after the taps are adjusted. To obviate the inconvenience of stopping to change or refill that would be necessary in longer operations, Brunner, Boisgiraud, Dancer, Muencke, and others have contrived double aspirators so connected that each vessel is alternately above and below, and one or other always ready for use. The aspirating bottles may be mounted on a common axis as in Dancer's swivel aspirator Fig. 4 (Chem. News, 1864, 10, 295). These swivel aspirators are very convenient, but the difference of water-level in the two bottles is not under the control of the operator and varies between the height of one bottle and a very small minimum.

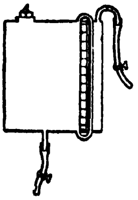


FIG. 3.

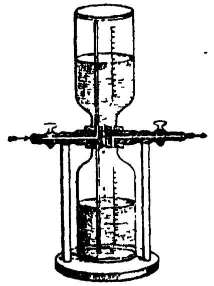


FIG. 4.

Figs. 5 and 6 show an arrangement devised by the author, which has certain advantages. The bottles A and B are connected as shown, being raised and lowered alternately. The four-way tap C (shown larger in Fig. 6) has its index I turned towards the upper bottle in aspirating and towards the lower bottle in blowing. It is made from a good gas tap by boring up the centre of the plug at F, leading out the hole at G. A small piece of metal H is then fitted and soldered diagonally where the holes cross, a piece of tubing K soldered on to the socket of the tap, and an index I above the plug.

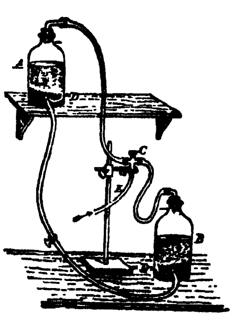


FIG. 5.

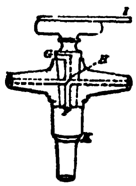


FIG. 6.

Paraffin wax is used to adjust the bottles for exact measurement, and to obtain a fine adjustment below at D, as well as above, by a mark on the neck of the bottle. The proper quantity of melted wax is run through a wide tube into the warm bottle slightly tilted. A passage from the tubulure to D at the side of the bottle is secured by pushing an indiarubber tube through the tubulure and fixing it in the proper position before the wax is run in, and after the wax is quite solid this tube is drawn out. The passage should be curved, so that on emptying the bottle of water the water runs out to the mark at D. The bottles are then adjusted by weighing their content of water between the marks and adding or removing paraffin till at the standard temperature and pressure they hold the exact quantity of water corresponding to the volume required. In successive weighings of bottles so adjusted the differences should not exceed 0·1 gram. To avoid loosening of the wax from direct contact with the glass, the bottles should be preserved from changes of temperature and from mechanical vibration, &c.

Constant or automatic aspirators. Instruments of this class have been invented by Guthrie (Phil. Mag. [4] 15, 64) and by Bonny (Winkler's Technical Gas Analysis, trans. by Lunge, 17). In each of them a pipe from the water supply leads a constant stream of water into a vessel, which, when full, is emptied by a siphon, whose tube is of larger size than the supply pipe. The arrangement thus acts on the principle of the intermittent siphon, and the vessel is filled and emptied at regular intervals. In Bonny's instrument these are registered by a simple mechanism, and the total volume passed is known on measuring the volume passed in one operation.

The Sprengel and injector pumps may be used as constant aspirators (*v.* FILTER PUMPS). By means of a collecting box attached below the pumps to allow the gas and water to escape at different levels, the gas may be measured by passing it through a small gas meter (Davis, J. Soc. Chem. Ind. 211).

J. Grossman (Winkler's Industrie-Gase, 218) has invented a small mercurial aspirator, on the principle of the Geissler pump, with two reservoirs, which are alternately raised and lowered. It is fitted with registering apparatus.

In testing air and gases from confined places, works, &c., Angus Smith, Davis, and others have used small pear-shaped aspirators of indiarubber. These are emptied by simply squeezing in the hand. The air escapes by a valve, of which the simplest is a small slit in the rubber connecting tube, opening outwards like a Bunsen's valve. The rubber recovering its form draws a certain volume of gas through the testing apparatus, and it is easy to ascertain approximately the total volume of gas corresponding to any given number of times the aspirator has been filled. Another larger aspirator of this class is of bellows form, like a concertina, the folding part being of indiarubber. This aspirator is frequently used for filling by displacement jars or bottles with gas to be tested. The common single-barrel air pump or apparatus, on the same principle, is also applied in this manner as an aspirator.

At the British Association Belfast meeting, 1874, the late Prof. Andrews showed how an ordinary wet gas meter could be converted into an aspirator by applying motive power to the hollow axis of the drum, thereby causing it to suck in air at the inlet side and at the same time to measure the air on the meter index. Using mercury as liquid in a cast-iron meter, a similar arrangement forms the basis of the Barr and Stroud air pump applied in the evacuation of bulbs for electric lighting lamps (J. Soc. Chem. Ind. 1896, 640; Eng. Pat. 13188, July, 1895).

T. F.

ASPIRIN. Trade name for acetyl salicylic acid $C_6H_4(COOH)O\cdot CO\cdot CH_3$, used as an antirheumatic, and in the treatment of headaches, feverish colds, &c. Is hydrolysed in the intestine forming sodium salicylate.

ASPIROPHEN. Trade name for amino acetphenetide acetyl salicylate.

ASQUIRROL. Trade name for mercury dimethoxide.

ASSAYING. Assaying, 'the trial of metals,' a term originally applied only to the testing of gold and silver, is now usually extended to the determination of the quantity of the valuable metal in an ore or metallurgical product. It is also sometimes taken to include the estimation of any element which may prejudicially affect the value of the ore, but it is more usual to discuss this together with such work as the complete analysis of ores, slags, furnace materials, fuel, &c., under the heading of 'metallurgical analysis.' A brief account of some of these sections is given below.

The art of assaying is of great antiquity. The use of the touchstone for testing gold in India was referred to by Mathuranatha (Hist. of Hindu Chemistry, by Ray, ii. 231), and was probably known in the Greek world at least as early as B.C. 700, when the first electrum or gold-silver coins were manufactured. At any rate the touchstone found its way into Greek mythology. The testing of gold alloys by cementation was described by Pliny, by Strabo, and in the eighth century A.D. by the Arabian Geber, who was also familiar with the method of cupellation, and is reputed to have discovered nitric acid. The parting assay of gold with the aid of this acid is referred to in a decree of Philippe de Valois in the year 1343, confirming its use in the French Mint. Alloys of silver with copper were tested by observing the degree of blackening caused by heat in the Roman Mint under the Republic (Rochon, Essais sur les Monnoies, 17, 1792).

It is probable that ores were not valued except by inspection until the Middle Ages. The first clear references to ore-assaying are to be found in the anonymous little books entitled Probierbüchlein, which were published in Germany early in the sixteenth century, and in the writings of Biringuccio, Agricola, and Ercker in the same century, but the art was evidently regarded by these authors as already ancient at the time at which they wrote. Ercker, writing at Frankfort in 1580, describes the fire-assays not only of several different kinds of gold and silver ores, but also of the ores of copper, lead, tin, antimony, iron, mercury, and bismuth. Assaying by means of 'wet methods,' volumetric, gravimetric, and electrolytic, is of comparatively recent introduction (excepting the parting assay of gold), but has now in great part superseded the ancient processes involving the use of furnaces.

Sampling.—Whether the material to be assayed is a portion of a vein underground, a heap of broken ore, pigs of metal, or a delicate piece of jewellery, in every case a representative sample must be obtained. In the case of ore *in situ* underground, pieces are taken from a number of different points and either mixed or examined separately. Ore which can be moved is reduced in bulk either by hand or by machinery, and is generally crushed finer between each successive reduction in bulk. Every second, fifth, tenth, or twentieth shovelful or car-load may be set aside as a sample, or the whole heap may be made into a perfect cone, which is flattened and divided into four quarters along two diameters. Two opposite quarters are removed and mixed, and the process of 'coning and quartering' repeated as often as necessary. A heap or vat of ore or tailings, which must be sampled without being moved, is pierced at regularly spaced intervals by a sampling tube which resembles a cheese-taster, and withdraws a cylindrical sample extending to the bottom of the vat or heap.

In automatic sampling machines, which are much used in Western America, the crushed ore is made to slide down an inclined plane or rotating cone, and a portion of the stream of ore is deflected and set aside as a sample. Those machines are preferred which momentarily take the whole stream of ore at regular intervals of time. A stream of pulp is sampled by the passage through it from side to side or from top to bottom, at regular intervals of time, of a receptacle which is large enough not to overflow while the sample is being intercepted. The pulp sample is then filtered and dried. Further reduction in the laboratory is effected by coning and quartering or by a machine such as the *riffle* or *sampling tin*, which consists of a series of metal troughs arranged side by side and fastened at equal distances from each other. A stream of ore let fall on it is in part retained by the troughs and in part passes through.

The final grinding of the ore is effected by means of an iron pestle and mortar, or of a large hammer with a curved face sliding on an iron plate (or *buckboard*), or by some form of rolling or grinding mill. The crushed ore is passed through a sieve, the fineness of which varies according to the ore and the method of assay. If a panning test is required, a 20-mesh sieve (*i.e.* one with 20 holes to the linear inch) suffices. For most fusions, *e.g.* dry lead assay, a 60-mesh sieve is used. Gold ores are crushed through an 80- or 100-mesh sieve, and in the case of tin ores and of telluride ores of gold, the best results are obtained by using 120-mesh sieves. Before it can be passed through a fine sieve, the ore must be dried, so that the *moisture* is determined on coarsely crushed ore by drying at 100° on a water-bath, or, if the dry material is not likely to be affected in any way by a somewhat higher temperature, it is heated on a sand-bath. In crushing rich gold and silver ores, mint sweepings, &c., pieces of metal are found which become flattened out and are caught on the sieve. These 'metallics' are treated separately, and the value calculated on the weight of ore from which they were derived.

The dried and crushed sample is thoroughly mixed by means of a spatula in a basin, or on rubber-cloth, before the portion required for assay is weighed out. If stored in a bottle or tin, the movement of the vessel causes the heavy particles to settle, so that the material at the bottom becomes richer than that at the top.

Ingots of metal are sampled by cuts taken from the corners or edges, as in the case of refined gold and silver, or by drillings from a number of different spots, as is sometimes done in the case of iron and steel and of unrefined gold and silver Pigs of argentiferous lead are sometimes sampled by drillings or saw cuts. Base gold and silver ingots, and in many cases ingots of steel and pigs of lead, are melted and stirred, and a portion dipped out and granulated by pouring into water, or cast into a little ingot. Coins are sampled in various ways, silver coins being seldom uniform in composition. The simplest method applicable to all is to roll them out and cut them into a large number of little pieces, so that all parts of the coin may be represented in the portion taken for assay. This method is adopted in the Philadelphia Mint, but is not in general use, other more complicated methods being preferred. Gold and silver wares are usually pickled, and are richer on the surface than in the interior. In sampling them, it is accordingly necessary to remove the outside by scraping and then to scrape off a portion of metal for assay.

The *preliminary examination* of ores includes careful inspection, which is all the more useful if some comparatively large pieces are included in the sample. The proximate constituents, such as quartz, pyrites, magnetite, galena, &c., are thus observed, and the proportions in which they are present roughly estimated, this information being required in making-up furnace charges. Frequently a concentration test is made in a miner's pan (a flat-bottomed sheet-iron pan about 20 inches in diameter, and 3 or 4 inches deep, with sloping slides) or a vanning shovel, or in any basin, pan, or even clock-glass available. For this purpose a portion of 25 grams or more is weighed out, stirred and shaken with water by a circular motion on the shovel, and the lighter particles rinsed away and caught in a basin. Finally by a combination of the circular motion, and a series of jerks, the denser particles are thrown up and the lighter ones washed down the shovel. The concentrates are examined with a lens or separated, dried, and weighed, or treated with acid, or examined by means of the blowpipe, or in other ways, in order to determine the presence or absence of elements likely to interfere with the method of assay chosen. The vanning shovel is used particularly with tin ores, but may be applied to any others. Panning tests are especially useful in the examination of gold ores, but are also required to determine the nature of the 'mineral' or compounds of the heavy metals in almost all ores. The test may be applied to half a gram of ore in a watch-glass, if no more can be spared.

The furnaces used by assayers are the muffle furnace, and the melting or wind-furnace.

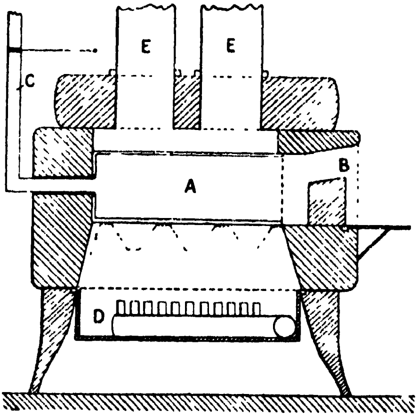


FIG 1.

The *muffle furnace* consists of a small oven or muffle of refractory fireclay open at the front, and having an arched top. It is heated by coal, coke, oil, gas, or electricity. Muffles vary in size according to the amount of work to be done, but those used at the Royal Mint may be considered full size. Sectional views of one of these furnaces are shown in Figs. 1 and 2. The muffle A is 14½ inches long, 8¼ inches wide, and 5 inches high, inside measurements, with walls about ⅜ inch thick. The mouth is closed by the firebrick B and by a sliding plate resting on B. Air enters through holes in the sliding

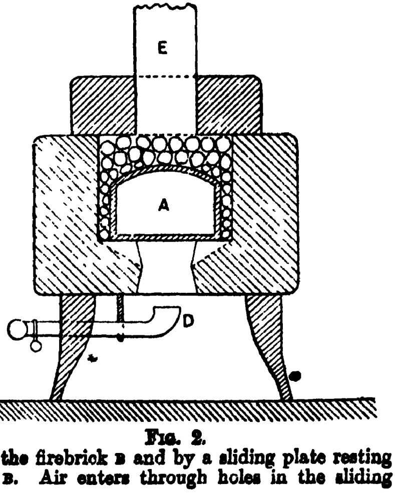


FIG. 2.

plate and passes out at the back through the tube O, which has a sliding damper and leads into the main flue. The fuel is ordinary gas, supplied by a row of bunsen burners D, and complete combustion of the gas may be aided by clay fireballs surrounding the muffle. The flues E E carry off the waste gases. The furnace walls consist of firebrick bound with iron and covered with a thick layer of magnesia and asbestos to check radiation. No chimney stack or forced draught is required for this furnace.

A *melting furnace* adapted for the use of coke as fuel and suitable to make fusions in assay operations, is shown in section in Fig. 3, in which A is the fireplace, B the flue, C the ashpit, D the damper, and E the firedoor. The most useful size of the fireplace is about 9 inches square, and about 10 inches in depth from the firebars to the flue. The furnace is built of brick and lined with firebrick. It is bound with angle iron or covered with iron plates bolted together and furnished with tie rods. Gas-melting furnaces with natural draught or using a blast of air are less common. Fluxing crucibles consist of fireclay or, in the assay of galena, of wrought iron. They are of different sizes and shapes, the best-known being the Battersea (round, Cornish, and triangle), French, Hessian, and Colorado crucibles, the last-named being used for making fusions in the muffle, a common practice in America. Most crucibles require careful annealing before being used. Roasting dishes made of fireclay are for the roasting of ores; fireclay scorifying dishes or scorifiers are used in the process of scorification; cupels of various shapes and sizes are made of compressed bone-ash or magnesia, and are required in the assay of the precious metals. The bone-ash cupels may be made by the assayer, and must be carefully dried before use. Magnesia cupels are usually bought ready-made.

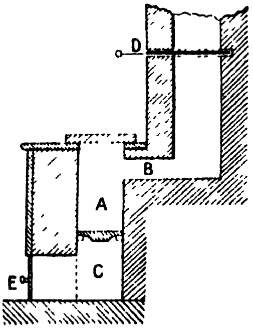


FIG. 3.

The *reagents* used in fire assay may be classed as fluxes, agents for reducing, oxidising, sulphurising, and desulphurising, and covers to protect the contents of the crucible from the action of the air, furnace gases, &c. Generally speaking, an ore consists of compounds of a heavy metal or metals (the mineral), together with a quantity of earthy materials, such as quartz, silicates, &c. (the gangue). It is required to reduce the valuable constituent to metallic form, and to incorporate the remainder of the ore in a fusible slag, through which the particles of metal may settle to the bottom, where they collect in the form of a button. Sometimes a regulus or matte (sulphide of a heavy metal) or a speise (arsenide of a heavy metal) forms a separate layer between the metal and the slag, and a cover, say, of common salt, may be provided which is lighter than silicate slags and floats on the top. On breaking open a cold crucible in which a fusion has been made, there are, therefore, frequently four layers.

The principal fluxes used are sodium carbonate, which forms fusible mixtures with acid (siliceous) ores, and also acts as a desulphuriser, converting pyrites into a mixture of sulphides of iron and sodium which does not form a regulus, but is dispersed through the slag. Carbonate of soda is now generally used in the anhydrous form, Na_2CO_3, but the bicarbonate, which gives up half its carbonic acid without fusion is also suitable. Soda crystals give up their water of crystallisation with ebullition, and are not suitable unless previously dried. Basic ores require borax, which forms fusible mixtures with oxides of iron, lime, &c.; and increases the fluidity of most charges. Crystallised borax powder on heating swells up enormously, gives up its water and fuses into a glass. The swelling may occasion loss in the assay if the crucible is too full. To avoid this, borax glass may be used, which is equivalent to about double its weight of ordinary borax. Litharge is a useful flux, especially for oxides of iron, copper, &c., but attacks and corrodes the crucibles. Fluorspar is sometimes used, especially for phosphates. Sand is often required to protect the crucible from attack by basic ores.

The reducing agents are carbon (charcoal powder or lampblack), flour, tartar or argol (crude hydrogen potassium tartrate), and occasionally potassium cyanide. One part of charcoal is about equal to two parts of flour or five of tartar, but tartar also acts as a flux, being converted by heat into carbon and potassium carbonate. Black flux is a reducing mixture made by deflagrating one part of nitre with two and a half parts of argol.

The chief oxidising agents, which are also desulphurisers, are hot air, litharge or red lead, and nitre. Iron is often used as a desulphurising agent. The ordinary materials used as covers are borax and common salt.

The *balances and weights* do not differ, as a rule, from those used in ordinary chemical analysis, the most notable exception being in the case of those used in the assay of gold and silver. The proportion of these metals present in ores is reported in troy ounces, pennyweights, and grains per ton, or sometimes in ounces and decimals or in pennyweights and decimals. The weight of ore taken for assay accordingly contains as many milligrams as there are ounces troy in a ton (29,166 in a ton of 2000 lbs., and 32,666 in a ton of 2240 lbs.). This weight of 29·166 grams is called an *assay-ton* (or A.T.), and boxes of weights made up of assay-tons and decimals are used by many assayers. Then the gold extracted from the sample of ore is weighed in milligrams, and can be reported without calculation. In the assay of gold bullion the weights commonly range from '1000' downwards, where 1000=0·5 gram or some other unit such as 5 grains. Much tedious calculation is avoided by thus marking the weights so that their face-value gives at once the result of the assay. Again, in assaying silver by precipitation as chloride

(India Mint method, see p. 419), since 18·815 grains of pure silver are contained in 25 grains of chloride, it follows that if 18·815 grains of an alloy be always taken for assay, and the resulting chloride be weighed out with a series of weights the largest of which is marked 1000, and is equal to 25 grains, and the others are marked correspondingly, then the subsidiary weights of this series will indicate the result of the assay without calculation. A similar series can, of course, be arranged for any special purpose.

The balances used for weighing gold and silver in bullion assays are light and delicate, taking about 2 grams as their maximum of weight, and turning to one hundredth of a milligram. Usually, one division of the ivory scale is made equal to 0·05 mg. Balances for weighing the parted gold in ore assays are still more delicate. The maximum weight which they can carry is only 1 gram or even less, and they turn with one-hundredth or in some cases only one five-hundredth of a milligram. Milligram and half-milligram riders are used, but the final reading is always based on the deflection from the zero position of the pointer, measured by the number of divisions on the ivory scale covered by the swing. At the present day short beams of 6 inches, 4 inches, and even 8 cm. in length, are in use, so that the balances are very rapid in action in spite of their sensitiveness.

In quantitative blowpipe work on gold and silver, it has been found possible to dispense altogether with a delicate balance, and to use an ivory scale (Plattner's scale), by which the diameter of the bead of metal is accurately measured. The principle has been extended in the assay of poor materials, and beads of microscopic dimensions are placed on the stage of a microscope and measured by means of a micrometer eyepiece. In this way L. Wagoner (Trans. Am. Inst. Mining Eng. xxxi. 1901, 798) obtained a close approximation to the weight of beads of silver of 0·02 mm. in diameter, which weighed about 0·00004 mg.

The above summary has special reference to the requirements of a laboratory for making dry or fire assays. For wet assays, the apparatus and reagents are those of the ordinary analytical laboratory (*v.* ANALYSIS).

In all methods of assaying, wet or dry, time must be considered as well as accuracy. It is sometimes important to arrive at a result in the course of an hour or less, and some of the methods described are intended for such emergencies, when extreme accuracy must be sacrificed. It is also necessary to observe that assay methods are intended to be comparative, and wherever it is possible check assays on similar materials of known composition should be made side by side with the assays of ores or other bodies requiring examination, and a correction applied to the results. In the following pages, only methods in common use in assay offices are described. The methods of ordinary analysis are generally omitted or made the subject of brief reference.

Aluminium. There are no special methods of assaying the ores of this metal. The silicates are broken up, and the silica removed as usual, and the acid solution of the bases is treated so as to separate the metals contained in it. Aluminium is precipitated and weighed as phosphate $AlPO_4$, or oxide Al_2O_3. It is sometimes weighed as oxide together with oxide of iron Fe_2O_3, and also P_2O_5, if these constituents are present in the ore. The last mentioned constituent is of course combined as phosphate. The phosphorus and iron are then determined, aluminium being estimated by difference (Low's Technical Methods of Ore Analysis, 1st ed. 22).

Antimony. The antimony in ores may be determined by fusion with cyanide of potassium or with iron (avoiding excess) and black flux, but the results are unsatisfactory. The sulphide of antimony in an ore may also be approximately determined by charging 500 grams of ore broken to nut-size into a clay crucible with a perforated bottom. This crucible is fitted into another of about the same size, and the joint carefully luted. A cover is also luted on, and the whole is slowly raised to a red heat. The sulphide of antimony fuses and liquates into the lower crucible, from which it can be detached when cold, and weighed. The fused sulphide of antimony, if pure, contains 71·7 p.c. of the metal. The valuation of antimony sulphide ores is usually effected, according to Bedford McNeill (Berenger's Assaying, 11th ed. 226), by having recourse to the ordinary smelting operation, which is to be used in treating the ore on the large scale. Charges of about 20 kilos. of ore are used for the valuation.

The wet methods of estimation of antimony in ore are far more accurate than those referred to above. The ore is fused with sulphur and sodium carbonate, and then digested with water. A solution of an alkaline sulpho-compound of antimony is thus obtained, from which a mixture of antimony and arsenic sulphides and free sulphur is precipitated by the addition of dilute hydrochloric acid. After the arsenic has been separated, the antimony sulphide is weighed or is oxidised by fuming nitric acid, and weighed as Sb_2O_4. Ores may also be attacked by hydrochloric acid. The antimony in the separated sulphide may be estimated volumetrically, dissolving the sulphides in hydrochloric acid and chlorate of potash, warming to expel the chlorine, adding an excess of potassium iodide, and titrating with thiosulphate of soda (J. Soc. Chem. Ind. xv. 255).

Arsenic. The determination of arsenic in ores and metallurgical products is usually made by Pearce's method, which consists in fusing about 0·5 gram of the ore with 5 grams of a mixture of equal parts of sodium carbonate and nitre, dissolving out the soluble arsenates of the alkalis and precipitating the arsenic in a neutral solution by means of silver nitrate. The precipitated brick-red silver arsenate Ag_3AsO_4 is filtered off, dissolved in nitric acid, and the silver in it determined by Volhard's thiocyanate method. The amount of arsenic present can then be calculated (Low's Ore Analysis, 41). Small quantities of arsenic in metals and minerals may be separated by distillation with ferric chloride and calcium chloride in a hydrochloric acid solution, the distilled arsenious chloride being condensed in a vessel of cold water (Berenger's Assaying, 384). (For arsenic in steel, see p. 417.)

Bismuth, if present in an ore in the metallic state, may be determined by liquation, the method of procedure being similar to that used in liquating sulphide of antimony (*q.v.*). The bismuth in an ore may also be determined by fusing it with fusion mixture, common salt, and cyanide of potassium. These methods are inexact, and bismuth is usually determined by being weighed as Bi_2O_3 after precipitation as carbonate, or as BiOCl on a weighed filter or a Gooch crucible after being dried at 100°. Bismuth in metallic lead is precipitated and weighed as BiOCl, and in metallic copper it is detected by the colour given to lead iodide. (For estimation of bismuth in copper, *see* p. 414.)

Chromium occurs in chrome-iron ore and sometimes in other iron ores, in pig-iron and in steel. Small quantities of chromium in iron ores, after separation from other metals and earths, are precipitated by lead acetate in an acetic acid solution, and weighed as $PbCrO_4$, or, in the alternative, reduced by sulphurous acid and the chromium precipitated from the green solution by means of ammonia and weighed as Cr_2O_3. Chrome-iron ore is assayed by a volumetric method based on the oxidation of ferrous iron by chromium in the form of chromate. The chromium is oxidised by fusion with peroxide of sodium (J. Iron and Steel Inst. xlviii. 153). The ferrous iron is added in the form of a weighed amount of ferrous ammonium sulphate or of a weighed amount of metallic iron dissolved in sulphuric acid. The excess of ferrous iron present in the solution containing the chromium is titrated with permanganate. Chromium in steel is precipitated and weighed as chromium phosphate (Chem. News, lvii. 1888, 153), or as chromic oxide Cr_2O_3.

Cobalt. *See* **Nickel**, p. 418.

Copper. The principal ores of copper are (*a*) native copper; (*b*) sulphide ores, copper pyrites or yellow ore, erubescite or purple ore, grey copper ore, &c.; (*c*) oxidised ores, malachite, silicate of copper, &c. The treatment of copper ores results in the production of copper matte or regulus containing from 30 to 50 p.c. of copper, and cement copper or copper precipitate, containing 70 p.c. or more of metallic copper. In addition to these materials, ordinary commercial standard copper, refined copper, and the alloys of copper require to be assayed.

The chief methods in use are as follows:—

(1) *Dry or Cornish assay*, long used in connection with the sale of copper ores, but applicable chiefly to mattes and rich sulphide ores. It is especially unsatisfactory when dealing with poor ores, but gives low results in all cases, the loss, according to Beringer, ranging from 2 p.c. of the copper present in the richest materials to 33 p.c. of the copper in 2 p.c. ore. It consists in fusing the calcined regulus for metallic copper and refining the copper. Rich oxidised ores are fused for metal at once. The amount of ore taken for assay is 400 grains, but with rich material only 200 grains or even 100 grains are taken. The fluxes vary with the nature of the ore, in which there may be too much sulphur and iron, as in copper pyrites, &c., or too little, as in grey copper. The following are examples of the charges:—

	A. Copper pyrites	B. Grey copper ore
Ore	200 grains	100 grains
Nitre	50 ,,	—
Lime	200 ,,	200 ,,
Fluorspar	200 ,,	200 ,,
Glass	150 ,,	150 ,,
Borax	150 ,,	150 ,,
Hæmatite	—	15–20 ,,
Sulphur	—	25–30 ,,
Argol	—	30 ,,

The charge is fused in a 'large copper' crucible at a low red heat, which is gradually raised. After about 15 minutes the charge is poured into a conical mould, and, as soon as the slag is solid, it is taken up by tongs, dipped into water, and allowed to dry. When treated in this way, the slag breaks up readily. The regulus is detached by a hammer and crushed to powder in an iron mortar. It should be reddish-brown in colour and contain about 50 p.c. of copper and 20 p.c. of iron. It is roasted in a Cornish crucible in the melting furnace or in a roasting dish in the muffle, at a low but increasing temperature, with continuous stirring at first. When 'sweet,' *i.e.* not smelling of sulphur, at a full red heat, it is mixed with a little charcoal powder, and re-roasted to decompose sulphates. It is then crushed again, if necessary, and fused in the same crucible with argol, borax, and sodium carbonate. A high temperature is required, and the charge is poured in about 15 minutes. The slag is detached and cleaned by a second fusion with more argol and sodium carbonate. The 'coarse copper' obtained in this way is refined by being charged into a very hot crucible and melted. The impurities are oxidised by the air and form a ring of oxides round an eye of copper. Then refining flux, which consists of a deflagrated mixture of nitre, argol, and common salt, is added, and 2 minutes later the copper is poured, and if it is found to be at 'tough pitch,' it is weighed. The slag contains copper, and must be cleaned. (For full details of the method, *see* Percy's Metallurgy, i. 1861, 454–478.)

(2) *Electrolytic assay of copper.* The weight of ore taken for assay depends on its richness, a convenient amount of metallic copper for electro-deposition being from 0·1 to 0·5 gram. When using this method or any of the other wet methods, the copper must first be brought into solution and usually separated from other metals. Oxidised ores may require merely to be treated with hydrochloric acid. Sulphide ores, mattes, copper precipitate, &c., are attacked by nitric acid, evaporated to dryness, and taken up by hydrochloric acid. Copper slags are fused with sodium and potassium carbonate (fusion mixture), and a little nitre, and are then digested with water and hydrochloric acid. The copper is precipitated from its hydrochloric acid solution by means of sulphuretted hydrogen or (after evaporation with sulphuric acid) by sodium thiosulphate, and the sulphides are filtered off and redissolved in nitric acid. The copper may also be separated from other metals by adding sulphuric acid to the nitric or nitrohydrochloric acid solution and boiling off the volatile acids. The solution is cooled, diluted and filtered, and the copper precipitated at a boiling temperature with aluminium foil. For the electrolytic assay, the

solution obtained in one of these ways is diluted, warmed, and filtered into a 200 c.c. flask, and made up to about 100 c.c., of which from 2·5 to 5 p.c. should be nitric acid. Platinum electrodes (spiral and weighed cone or cylinder) are then placed in position, and a current from two Daniell cells in series is passed through for 16 or 17 hours. The cylinder is removed from the colourless solution, washed with water and afterwards with alcohol, dried in a water-oven, and weighed. The copper precipitate should be salmon-red in colour. The solution still contains a little copper, which is estimated colorimetrically, ammonia being added, and the colour, after filtration, compared with those of standard solutions containing known amounts of copper. Silver, mercury, bismuth, arsenic, and antimony interfere with the process, being deposited with the copper. Mercury, however, is separated on dissolving the sulphides in nitric acid. Bismuth turns the copper dark grey, but is not deposited until most of the copper has been thrown down. Arsenic and antimony darken the copper deposit, but may be driven off by heating to dull redness. Lead is deposited at the anode as a dark-coloured coating of PbO_2, and may be weighed in that form. The electrolytic assay is suitable for all materials containing copper (*cf.* ELECTROLYTIC ANALYSIS).

By rapidly rotating the cathode a coherent deposit can be obtained even when a strong current of 10 to 12 amperes per 100 sq. cms. of cathodic area instead of the usual current of 0·5 to 1·0 ampere is used. The time required for the deposition of the copper may thus be shortened to a few minutes (Amer. J. Sci. 1903, xvii. 320, xviii. 56; J. Amer. Chem. Soc. xxv. 896; Chem. Soc. Trans. xci. 373).

(3) *The volumetric assay of copper.* There are two main processes—the potassium cyanide and the iodide methods. Both are in wide use in the assay of ores, alloys, &c. In preparing to use these methods, the copper is brought into solution, and may be separated from other metals, &c., as already described, with any further precautions necessary to remove special impurities. With ordinary pyritic ores, however, containing no zinc, silver, nickel, or cobalt, it is sufficient, in preparing for the cyanide process, to heat the ore gently with concentrated nitric acid to which a little sulphuric acid has been added. It is then diluted, an excess of ammonia or of Na_2CO_3 added, the bulk made up to some convenient amount such as 300 c.c., and the solution titrated with potassium cyanide. The blue solution is decolourised, and when overdone changes to a straw-yellow colour. The results are affected by time, temperature, degree of dilution, and by the amounts of ammonia and of ammonium salts. The conditions of the check assays on pure copper and those on ores, &c., must therefore be identical, and ferric hydrate, for example, must be present either in both or in neither. If, however, the solution is free from ammonia and ammonium salts, and is made alkaline with sodium carbonate, the effects of time, temperature and degree of dilution are much reduced, while ferric salts do not affect the result unless present in such amount as to mask the end reaction. The standard cyanide solution, which decomposes somewhat rapidly, contains about 42 grams KCy to the litre, and 100 c.c. of this is equivalent to 1 gram of copper. The reaction, according to Beringer, is represented by the equation:

$$CuSO_4+4KCy=2KCy\cdot CuCy_2+K_2SO_4.$$

The quantity of copper usually present in an assay is about 0·5 gram. At the finish the effect of an addition of 0·5 c.c. of cyanide is readily observable. Zinc, silver, nickel, and cobalt interfere with the assay, and must be removed before titration.

In the iodide method, the alloy or the sulphide of copper separated from the ore is dissolved in nitric acid, evaporated almost to dryness in order to expel nitrous fumes, and diluted. The nitrous products may also be destroyed by urea. The solution is then filtered if necessary, and carefully neutralised with sodium carbonate, avoiding excess. One c.c. of acetic acid is then added, which should be enough to redissolve the precipitated copper. Next, after cooling the flask, an amount of about 5 grams of potassium iodide crystals is added (or not less than ten times the weight of the copper present); the solution is diluted to a fixed amount, say 50 c.c.; and the liberated iodine is at once titrated with a solution containing 39·18 grams sodium thiosulphate (equivalent to 10 grams of copper) to the litre. The reactions are represented by the equations:

$$2CuSO_4+4KI=Cu_2I_2+2I+2K_2SO_4$$
$$2Na_2S_2O_3+2I=2NaI+Na_2S_4O_6.$$

When the yellow colour is almost discharged, 2 c.c. of fresh starch solution is added, and the addition of the thiosulphate continued drop by drop until the blue colour disappears and does not return within 2 or 3 minutes. The effect of one drop or 0·05 c.c. of standard solution, equivalent to 0·5 mg. copper, is observable. The solution is standardised with pure electrolytic copper. Ferric acetate, arsenic, lead, and large quantities of sodium acetate may interfere with the titration. According to J. W. Westmoreland (Beringer's Assaying, 441), sodium acetate counteracts the interference of arsenic and bismuth, and the bad effect of large quantities of sodium acetate is removed by doubling the amount of potassium iodide added. Iron, if present, is precipitated by ammonium phosphate (J. Soc. Chem. Ind. v. 48). Instead of neutralising with sodium carbonate and acidifying with acetic acid, an addition of 20 c.c. of a saturated solution of zinc acetate may be made (A. H. Low). In order to dispense with the large quantities of expensive potassium iodide required in the ordinary method, Moir proposes (J. Chem. Met. and Mng. Soc. of S.A., vol. xviii., Nov. 1917, p. 133) to add a slight excess of sodium thiosulphate to the usual very faintly acid solution of cupric acetate, and to titrate back with *N*/10-iodine, of which only a small quantity will be required.

The colorimetric method of assaying copper is sometimes used in the case of very poor ores, or generally whenever the quantity of copper present is small. Reference has been made to it above.

Examination of commercial copper. Electrolytic and Lake copper are generally nearly pure, but some of the metal sold contains as much as

2 or 3 p.c. of impurities. The most important of these are arsenic, lead, nickel, oxygen, and phosphorus; but antimony, bismuth, cobalt, gold, iron, selenium, silver, sulphur, and tellurium may also be present. The impurities to be looked for in copper which has passed a high conductivity test are mainly bismuth, selenium, and tellurium. Arsenic and phosphorus are separated as iron arsenate and phosphate mixed with acetate. Gold and antimony are separated by dissolving the copper in nitric acid, and silver is precipitated as chloride or bromide from a nitric acid solution. It may be collected in a precipitate of lead sulphate Nickel is left in solution by precipitating copper electrolytically, or by sulphuretted hydrogen in an acid solution. Lead is detected by the blackening of the anode in the electrolytic assay, and is estimated as sulphate or chromate.

The methods of determining oxygen may be classified in two groups (J. Inst. Metals, vii. 1912, 232):—

1. The estimation of cuprous oxide.
2. The estimation of total oxygen.

In Hampe's method (Zeitsch. anal. Chem. xiii. 1874, 215) of estimating the amount of cuprous oxide in copper, the copper is dissolved in cold dilute silver nitrate solution free from acid. The equations are as follows:—

$$Cu+2AgNO_3=Cu(NO_3)_2+2Ag$$

$$3Cu_2O+6AgNO_3+3H_2O$$
$$=2Cu(NO_3)_2+2Cu_2(HO)_3NO_3+6Ag$$

The copper existing as Cu_2O is found by multiplying the copper in the precipitate by $\frac{3}{2}$. The results are satisfactory.

Total oxygen is estimated by heating thin strips or bright turnings of copper to redness in a stream of hydrogen and weighing the water produced, or, better still, the residual copper. In the latter case, as mirrors of arsenic, antimony and bismuth may be formed, it is necessary to weigh the tube and copper together.

Bismuth is separated, according to Beringer, by precipitation by sodium bicarbonate. After redissolving in sulphuric acid, it is boiled with sulphurous acid and potassium iodide, and the bismuth in the yellow solution estimated colorimetrically. Tellurium and selenium (J. Amer. Chem. Soc. xvii. 280) are precipitated as iron tellurite and selenite by additions of iron nitrate and ammonia. The precipitate is redissolved in HCl, tartaric acid and potash added, and a current of sulphuretted hydrogen passed. The selenium and tellurium are subsequently precipitated by a current of sulphurous acid in a hydrochloric solution, and parted by boiling with potassium cyanide.

Gold. Gold is generally in the metallic state in its ores, either in the form of grains, scales, pellets, &c., in loose alluvial gravels, or in various forms embedded in quartz or other gangue in veins. It is frequently associated with iron pyrites, blende, &c., but the only native compounds are the tellurides. Besides these, the auriferous materials to be assayed comprise tailings or residues of ores after treatment, copper bottoms, pig lead, unrefined bullion, which contains silver, copper, and other metals, fine (*i.e.* refined) gold, and the commercial alloys used for coinage, plate, &c. The assay of gold ores and alloys is made with greater exactness than other assays, owing to the high value of the metal.

A *panning assay*, or concentration test is carried out as described on p. 409. The concentrates consist of 'black sand' or oxides of iron, titanium, &c., sulphides and arsenides, and sometimes grains of platinum. Free gold is sometimes visible, and is collected by grinding in a mortar with mercury, panning out the amalgam, and recovering the gold by distilling off the mercury or dissolving it in nitric acid. In either case the gold must be parted from the silver as described on p. 416. The panning assay of alluvial gold deposits is usually reported in grains of fine gold per cubic yard, which weighs about 3000 lbs., or 1½ short tons. In the panning assay, from 60 to 90 p.c. of the gold in the ore is usually recovered.

Ordinary gold ores are assayed by (1) the fusion or crucible method, or (2) the scorification method. In the *crucible assay*, the ore, crushed through an 80-mesh or finer sieve, is mixed with litharge or red lead, charcoal, or argol, and the necessary fluxes, and, fused in the melting furnace or, as in Western America, in the muffle. The amount of ore taken is usually 1 A.T. (assay-ton, see p. 410), but is sometimes only ½ A.T., and, in the case of poor tailings in which there are only a few grains of gold per ton, as much as 12 A.T. is taken and fused in several charges, the gold being finally collected into one lead button. The fluxes vary with the nature of the ore. The following are typical charges subject to very large variations to meet special cases:—

—	A. Silicious ore (grey or white with a little pyrites, &c.)	B. Basic oxidised ore (red or brown)	C. Pyritic ore
Ore . .	1 A.T.	1 A.T.	1 A.T.
Litharge or red lead	1 „	1 „	1 „
Charcoal .	1·2–1·5 grams	2·0 grams	0–1 gram
Sodium carbonate	1¼ A.T.	25 „	1 A.T.
Borax .	5–10 grams	10 „	10 grams

Sand is added to B and C if necessary for the protection of the crucible from corrosion. The borax is usually not mixed with the charge, but is added as a cover or charged in after the fusion has begun. The charge is well mixed and put into a cold crucible, which it must not make more than two-thirds full, and pieces of hoop iron or two or three tenpenny nails are embedded in the mixture. The crucible is gradually heated, a red heat beginning to appear after about 10 minutes, and a dull red heat not being attained for 30 minutes or more. Tranquil fusion results in 40 or 50 minutes from the time of charging in. The pot is then lifted out of the furnace, the nails removed, and the charge poured into a conical mould or allowed to cool in the pot, which is afterwards broken. When cool, the lead button is detached from the slag by hammering. The button should weigh at least 25 grams. If less than this amount of lead is reduced, a fresh charge is made up containing more charcoal, and any change is made in the fluxes which may seem desirable from the appearance of the slag. If the lead is hard or brittle, owing to the presence of impurities, it is usually scorified, sometimes with the addition of fresh lead, before being cupelled, as otherwise the loss of gold is increased.

The slag will contain gold and *a fortiori* silver if the conditions during fusion are favourable to oxidation of the metals. For this reason it is better to reduce almost all the litharge than to leave some of it in the slag, and the more readily oxidised metals—iron, manganese, &c.—must be reduced to their lowest oxides, ferrous oxide, &c. Practically all the copper, nickel, and other readily reducible metals will then be in the lead button. In the case of ores containing much copper, this is a disadvantage, entailing loss of gold in cupellation, and the copper may be removed from the ore by treatment with acid before fusion (with some loss of silver) or large quantities of litharge (6 A.T. of PbO to 1 A.T. of ore) may be added, and only a small part of it reduced. In the latter case the slag contains gold and silver, and is cleaned by a second fusion, with the reduction of more lead. A similar method of fluxing is used for telluride ores, an excess of litharge in the slag preventing tellurium from entering the lead button. Antimonial and arsenical gold ores are sometimes roasted with coal-dust in a reducing atmosphere, in order to remove the antimony or arsenic as a sulphide before fusion. An alternative method is to fuse with much litharge and enough nitre to oxidise the antimony with the formation of antimoniates. Sulphides may be roasted in air before fusion.

The lead button, rounded by hammering, is placed on a hot cupel in the muffle (*see* p. 10.)), which is kept at a full red heat. The lead melts and oxidises, and the litharge and other oxides are absorbed by the cupel, the gold and silver being left as a bead (or 'prill') on the surface. If the bead is large and contains much silver, it must be cooled gradually to prevent it from 'spitting' on solidification, by which part of the metals might be lost. The bead is cleaned, weighed, flattened, and parted by dissolution in boiling nitric acid in a porcelain crucible or test-tube. If less than two parts of silver are present to one of gold, the metals are not parted completely, silver being left in the gold, and it is convenient to have a greater proportion of silver present. It is, therefore, often necessary to melt the bead with more silver, the proportion varying with the size of the bead, as follows:—

Weight of gold	Silver required for parting
10 milligrams	40 milligrams
1 „	6 „
0·2 „ or less	2 „

A little extra silver is permissible, but if too much silver is present, there is a tendency for the gold to break up into very fine particles, which are difficult to wash without loss. The separation of these minute particles is avoided by dropping the bead into boiling acid, sp.gr. 1·2, when the parting will be completed in a few seconds. The parted gold is washed free from silver nitrate, &c., and is made firm and coherent for weighing by being annealed at a red heat. (For weights, balances, &c., *see* p. 410.) The silver is estimated by difference. The litharge, fluxes, &c., must be tested for silver and gold by running blank charges without ore.

In *scorification* about 0·1 or 0·2 A.T. of ore is mixed with 30 or 40 grams of granulated lead, and transferred to a dry scorifier. The charge is covered by a similar amount of granulated lead, and from 0·5 to 1 gram of borax is sprinkled on last. The scorifying dish is then charged into a muffle, which has been raised to a temperature of 1000°-1100°, or considerably above that required for cupellation, and the muffle is closed. As soon as the charge is melted down, the muffle is opened. The lead now oxidises, and the litharge, forming a ring of slag round the scorifier, oxidises the sulphides, &c., and slags off the earthy materials in the ore. As oxidation proceeds, the litharge encroaches on the 'eye' of metal, and at length covers it over. A pinch of charcoal powder is then added in tissue paper, and when the fusion is again tranquil, the charge is poured into a mould, and the slag detached. The lead is cupelled, and the assay finished as before.

In cupellation some gold and silver is carried into the cupel with the litharge, especially if tellurium, selenium, copper, &c., are present. The gold and silver are usually recovered by fusing the crushed cupel with litharge, charcoal, sodium carbonate, borax, and fluorspar, and cupelling the button of lead (see Lodge's Notes on Assaying, 112-169).

Assay of gold bullion and alloys. A piece of the metal to be examined is adjusted by cutting and filing to correspond in weight with a standard weight marked '1000,' which varies with different assayers between 5 and 10 grains, but is usually 0·5 gram. To the assay piece is added a piece of silver (free from gold) equal in weight to 2½ times (at the Royal Mint 2·1 times) that of the gold estimated to be present in the alloy, which, if not already known, can be ascertained by a rough preliminary assay or by the touchstone (*see* p. 416). The whole is wrapped in sheet lead, the weight of which depends mainly on the amount of copper to be removed, and varies from 8 to 32 times the weight of metal taken for assay. The lead packets are then transferred by means of tongs to cupels already raised to a bright red heat in the muffle, the current of air through the muffle is carefully regulated and the heat maintained. In from 10 to 20 minutes, a rapid passage of brilliant iridescent bands of colour over the surface of the button is observed to take place, and the buttons then appear to become colder, no longer glowing brightly with the oxidation of the lead. A few minutes later the muffle is closed to allow the buttons to set without loss by spitting. If copper is present in the assay pieces, however, this is not to be feared, and the charge can be drawn while the buttons are still molten. At the Royal Mint a charge consists of 72 assay pieces, which are charged in simultaneously by means of a divided metal tray with a sliding bottom and withdrawn simultaneously while still molten by means of a tray made of a mixture of graphite and clay, on which the cupels are placed. The buttons are cleaned by brushing, flattened on an anvil, annealed in the muffle or before a blowpipe, and reduced to a thickness of about 0·2 mm. by passage through a small pair of flatting rolls. The 'fillets' are again annealed and coiled into a spiral or 'cornet' by the finger and thimb.

The parting in nitric acid is effected either in glass parting flasks or in a platinum boiling apparatus. If parting flasks are used, an amount of about 2 oz. of nitric acid of sp.gr. 1·2 is heated in the flask almost to boiling, and the cornet is then dropped in and boiled until 2 or 3 minutes after the red fumes have disappeared. The acid is then poured off, and the gold, after being washed twice with boiling water, is boiled for a further 15 minutes with nitric acid of sp.gr. 1·2 or stronger. The acid must be free from silver, chlorine, &c.

The gold is again washed, and is then transferred to a porous crucible or 'annealing cup' by filling the flask with water, placing the cup over its mouth, and inverting it. The gold falls into the cup, and the flask is removed without agitating the water in the cup. The gold is then dried, annealed by heating to redness, and weighed. If no more than three parts of silver are present to one of gold, the cornet does not break up; and if enough is known previously of the composition of the bullion to make sure of this in the cupelled button, a platinum tray, containing a number of little platinum cups may be used. A cornet is placed in each cup, and the whole tray is immersed in nitric acid, and subsequently washed by dipping in and out of hot water. Less acid is used per assay piece by this method, and the boiling is more prolonged, 30 minutes in each of two acids of sp.gr. 1·23 being used at the Royal Mint.

In each batch of assays, two or more check assays on pure gold are made to determine the 'surcharge' or net sum of the losses of gold and the gain in weight due to the retention of silver. With alloys boiled separately in flasks, check assays are of comparatively little value (see Rose's Metallurgy of Gold, 5th ed. 470–498).

Alloys of gold and silver If the alloy contains enough silver to be parted by nitric acid, no difficulty arises. The silver is dissolved, precipitated by hydrochloric acid, and weighed either as chloride or as metal. If the silver is deficient in quantity, the alloy is melted with two and a half times its weight of cadmium under a cover of potassium cyanide and parted with nitric acid. The silver is precipitated and weighed as chloride, or determined volumetrically in solution by means of sulphocyanide. Sometimes the silver is determined by difference, the alloys being cupelled and weighed, and subsequently cupelled again with the addition of silver, and parted.

(For alloys containing *gold and platinum, see* p. 418.)

Assay by the touchstone. This ancient method consists in comparing the colour of the streak produced by a sample of gold of unknown composition on a black surface with those from a series of alloys of known compositions, after all have been treated alike with nitric acid. Any abrading surface on which the acid is without action can be employed for this purpose.

Iridium occurs alloyed with platinum, and finds its way into gold bullion. In the latter case, it is found with the gold cornet obtained in the bullion assay, adhering in the form of black scales or powder to that side of the gold which was originally nearest to the cupel. It can be estimated by dissolving the gold in *aqua regia*, the iridium remaining undissolved.

Iron. The dry assay of iron, made by fusing ores with fluxes in carbon-lined (brasqued) crucibles, is obsolete, and need not be described. The wet methods are volumetric, based on the oxidation of iron from the ferrous to the ferric state or on the converse reduction. Either the bichromate or the permanganate method is generally used to determine the total amount of iron in ores or the amount of iron present in the ferrous condition. The stannous chloride method is used for measuring the amount of iron present in the ferric state in an ore.

For the determination of the total amount of iron, the ore is passed through an 80-mesh sieve, and attacked by acids as usual. Most ores are oxides, carbonates, &c., and the iron in them is easily dissolved by hydrochloric acid.

Titaniferous ores are fused with acid potassium sulphate and dissolved in water and hydrochloric acid. If nitric acid is present in the acid solution, it is destroyed by evaporating to dryness with hydrochloric acid and taking up with hydrochloric acid and water, and the iron is then reduced by zinc, which gives a stream of hydrogen or (if titanium is present) by crystals of sodium sulphite in a neutral or slightly acid solution. As soon as the solution is colourless, the excess of zinc is removed, or the sodium sulphite decomposed by boiling with hydrochloric acid, and titration is carried out in a porcelain basin by means of a solution prepared by weighing out 4·39 grams of potassium bichromate to the litre, equivalent to 5 grams of iron according to the equation:

$$6FeCl_2+K_2Cr_2O_7+14HCl \\ =3Fe_2Cl_6+Cr_2Cl_6+2KCl+7H_2O.$$

Potassium ferricyanide (0·1 p.c. solution, freshly prepared) is used as an indicator, a drop from the assay solution being mixed with a drop of the test solution on a white glazed tile, from time to time. The end-point is reached when a colour is no longer produced. The solution of bichromate is standardised by means of piano wire, which contains about 0·4 p.c. of impurities.

The permanganate method is carried out in a sulphuric acid solution, the equation being:

$$10FeSO_4+K_2Mn_2O_8+8H_2SO_4 \\ =5Fe_2(SO_4)_3+2MnSO_4+K_2SO_4+8H_2O.$$

The standard solution is prepared by weighing out 2·82 grams of potassium permanganate per litre, which is equivalent to 5 grams of iron. The end reaction, the appearance of a pinkish tinge in the solution in the flask, is very sharp.

When the amount of ferrous iron only in the ore is required, the ore is dissolved in hydrochloric or sulphuric acid with exclusion of air. The ferric iron may be determined by difference, or, as a check, the stannous chloride method may be used, in which the yellow solution of ferric iron in hydrochloric acid is decolourised. The standard solution (20 grams of commercial stannous chloride per litre, acidulated with hydrochloric acid) is run into a boiling-hot solution of iron, and is standardised by means of a solution of ferric chloride free from nitric acid.

Analysis of iron and steel. The elements requiring estimation are carbon (graphite, combined carbon and total carbon), silicon, manganese, sulphur, phosphorus, arsenic, and, in special steels, chromium, nickel, tungsten, molybdenum, vanadium, &c. The total carbon is estimated by combustion, usually after removal of the iron by a cupric salt. The graphite is estimated by combustion of the residue after dissolving the iron in hydrochloric acid, by which the combined carbon is removed in combination with the hydrogen evolved, or more advantageously in nitric acid, by which the combined carbon is oxidised and retained in solution. The combined carbon is determined by the colour of a nitric acid solution compared with the colour of certain standard solutions containing known amounts of carbon. Silicon is weighed as silica after dissolution of the iron by acids or iodine. Sulphur is weighed as barium sulphate, after the iron has been dissolved in *aqua regia*, or it is evolved as sulphuretted hydrogen, which is absorbed by caustic soda, and decomposed by a standard solution of iodine. The excess of iodine is estimated by sodium thiosulphate.

Manganese is separated by precipitation with bromine in an ammoniacal solution after removal of the iron as basic acetate. The precipitated hydrated peroxide is heated strongly in a muffle and weighed as Mn_3O_4. There is also a colorimetric estimation, the steel being dissolved in nitric acid and the solution boiled with lead peroxide. The colour of the permanganate produced is compared with those of standard solutions. Phosphorus is precipitated by ammonium molybdate or magnesia mixture. Arsenic is separated by precipitation as sulphide in an acid solution, converted into arsenic acid and determined by precipitation by magnesia mixture.

(For the determination of the metals in special steels, *see* under the headings *Chromium*, *Nickel*, &c. For full details of the analysis of iron and steel and also of the complete analysis of iron ores, *see* Blair's Chemical Analysis of Iron, Campredon's Guide Pratique du Chimiste Métallurgiste et de l'Essayeur, 438–634, and Brearley and Ibbotson's Analysis of Steel Works Materials.)

Lead. Both dry and wet methods of assay are used. The dry assay is only applicable to rich ores and to concentrates, and even with these is less accurate than the wet methods. The ore is crushed through a 60-mesh sieve, mixed with sodium carbonate and argol, and fused in a wrought-iron crucible or in a clay pot with hoop-iron. Galena is reduced by the iron, and any oxides, sulphates, &c., of lead are reduced by the argol. Borax is sometimes added as a cover. The following are examples of the charges recommended by Percy:—

	1. Rich galena	2. Any galena, esp. poor ores	3. Phosphate ore	4. Cerussite
Ore . .	500 grs.	500 grs.	300 grs.	500 grs.
Sodium carbonate .	500 ,,	350 ,,	350 ,,	500 ,,
Argol (tartar)	50 ,,	100 ,,	100 ,,	100 ,,
Borax . .	—	150 ,,	30 ,,	30 ,,

The iron crucible is made red hot, cleaned, and allowed to cool. The charge is then transferred to it, care being taken to avoid loss by dusting, and the borax, or, if none is used, part of the sodium carbonate is added as a cover. A clay lid is also placed on the crucible. The charge is slowly heated for about 20 minutes, and is then poured into a mould, provided that all signs of effervescence have disappeared, and the mixture is seen to be in a state of tranquil fusion. The lead is found at the bottom. It is detached from the slag with a hammer, and is cleaned and weighed. The slag is examined for lead beads before being thrown away. Clay crucibles are used for phosphate and carbonate ores.

When the ore contains arsenic, a speise is formed which is found adhering to the upper surface of the lead, below the slag. It must be removed with great care to avoid loss of lead. The lead should be soft and malleable. The silver and gold in the ore are determined by cupellation and parting (*see* p. 415). The method gives results with pure ores which are about 1 or 2 p.c. too low. When the ore contains antimony, bismuth, copper, &c., these metals are in part reduced with the lead, and are weighed with it. If the lead button is hard, it is necessary to estimate the lead in it by weighing it as lead sulphate or otherwise, or to adopt wet methods of assaying the ore.

(For details of the dry assay of lead, see Percy's Metallurgy of Lead, 103–119.)

In the wet methods, oxidised ores are attacked by hydrochloric acid, followed by nitric acid, if necessary. Sulphide ores are treated direct with nitric acid. The lead is determined either as sulphate or volumetrically, by means of ammonium molybdate (Alexander's method). In the latter method (Eng. and Mng. J. April 1, 1893, 298), the mixture of nitric acid and ore is evaporated with sulphuric acid, diluted, boiled, and filtered. The lead sulphate in the residue is dissolved in hot ammonium acetate, acidified with acetic acid, raised to boiling, and titrated with a standard solution of ammonium molybdate, containing, according to Low, 4·25 grams per litre. The solution is standardised with pure lead foil. Tannin is used as an indicator, giving a yellow colour to a drop of the solution on a white glazed tile when the ammonium molybdate is in excess. If iron and calcium are present, it is better to separate the lead as sulphide and redissolve before titration (Low's Ore Analysis, 113).

Lead may also be determined in a feebly acid solution by adding an excess of potassium chromate and estimating the amount of excess by means of a standard solution of ferrous chloride. The reaction is the same as in the bichromate assay of iron, but in this case the end is marked by the appearance of a green colour in the test drops on the plate (Beringer's Assaying, 214).

Manganese occurs as MnO_2 in pyrolusite. Spiegeleisen, ferromanganese, and steel are also assayed for manganese. Either the ferrous sulphate assay or Volhard's volumetric process is generally used. In the latter method the manganese is precipitated by potassium permanganate in a boiling neutral solution. The precipitate, as far as numbers are concerned, is represented by the equation:

$$K_2Mn_2O_8+3MnSO_4+2H_2O$$
$$=K_2SO_4+5MnO_2+2H_2SO_4$$

About one gram of the ore or spiegeleisen is dissolved in hydrochloric and nitric acids, heated with sulphuric acid, and neutralised by the addition of an emulsion of zinc oxide in slight excess. All the iron is precipitated, and, after violently shaking the mixture, it is made up to 500 c.c., allowed to settle, and 100 c.c. of the clear supernatant liquid is drawn off, heated to boiling, and titrated. The end point is marked by the appearance of a pinkish tinge. (For the estimation of manganese in steel, *see* p 417.)

Mercury. The wet methods of assay are not satisfactory, and one of the distillation methods is usually employed. When a large percentage of mercury is present, a combustion tube of 18–20 inches long is used. It is sealed at one end and magnesite powder placed in it first, to a depth of 3 or 4 inches. Next a layer of ·2 inches of unslaked lime is added and then 5 or 10 grams of ore well mixed in a mortar with 10 grams of lime. The mortar is cleaned with more lime and the rinsings added to the tube and covered with clean lime to a depth of 3 or 4 inches. Finally, a loosely fitting plug of asbestos is inserted and the unoccupied portion of the tube is drawn out almost to a point and bent over at right angles, care being taken that no hollow in the glass is formed which might collect some of the mercury. The tube is placed in position in a combustion furnace and tapped until the mixture settles and leaves a free passage for gases throughout its length. The narrow opening is made to dip into a beaker of water, and the tube is heated, beginning with the asbestos plug and finishing with the magnesite, which yields enough carbon dioxide to sweep out the vapours of mercury. The time required for heating is about 30 minutes. While the tube is still red hot throughout its length, its end is cut off and dropped into the beaker. The mercury collects in the water, and is dried by blotting-paper and then in a desiccator and weighed in a porcelain crucible.

When only small quantities of mercury are present, Eschka's method is used (Dingl. poly. J. cciv. 74), in which the mercury is condensed on a weighed piece of gold. This is in the form of a basin made of thin sheet gold, used as the cover of a porcelain crucible and filled with water to keep it cool. The basin projects beyond the rim of the crucible, and usually weighs about 10 grams. From 0·2 to 2·0 grams of ore is mixed with 1–4 grams of iron filings, and heated in the crucible for 10 or 20 minutes, the flame being kept from heating the upper part. This may be done by fitting the crucible into a hole in a piece of sheet asbestos. The gold basin is then dried without the agency of heat, and weighed, the increase of weight representing the mercury.

Molybdenum in ores is estimated by precipitation as mercurous molybdate in a very slightly alkaline or neutral solution by means of mercurous nitrate. The precipitate is ignited in a porcelain crucible, either alone or with litharge, until the mercury is expelled. The increase in the weight of the crucible is taken as MoO_3, but if chromium, vanadium, tungsten, phosphorus, or arsenic is present in the ore, the ignited MoO_3 must be purified by further treatment or separated before precipitation. Molybdenum in steel is precipitated as ammonium phospho-molybdate.

Nickel and cobalt occur together in ores, the former more commonly and in greater proportion than the latter. They are usually assayed together. In the fire assay, the ore is roasted sweet and then fused with arsenic to form a speise. This is heated in air on a little clay dish in the muffle, and the metals oxidised successively, iron passing into the slag first, cobalt next, and then nickel, copper being left until last. The changes in colour of the borax slag show the progress of the assay. The slag is coloured brown while iron is passing into it, blue by cobalt, sherry-brown by nickel, and blue by copper. Gold is added to the speise after the elimination of cobalt if copper is present. The speise is weighed after each metal has been removed. The slag must be frequently examined and renewed, and great care and experience are needed to attain even approximate results.

The method is easier to carry out if copper is absent, and this metal is sometimes removed by precipitation with sulphuretted hydrogen in an acid solution before the speise is formed. If cobalt is absent, a weighed amount may be added, as otherwise it is difficult to observe the point at which nickel begins to pass into the slag after the removal of the iron. The arsenides in the speise have the formulæ Fe_2As, Co_2As, Ni_2As, and Cu_3As (Rhead & Sexton's Assaying, 187).

In the wet methods it is usual to roast the ore as a preliminary in order to remove the arsenic, sulphur, &c., and then to separate the nickel and cobalt from the iron, manganese, zinc, &c., by suitable methods. The nickel is precipitated as hydrate and weighed as NiO. Cobalt is often included in the nickel, but is separated if present in large quantities. A volumetric method depends on the interference by nickel in the titration of cyanide with a standard solution of silver nitrate. An alkaline solution containing caustic soda is used, and a little potassium iodide added as an indicator. An excess of a standard solution of potassium cyanide is added to a solution of nickel sulphate made alkaline (and precipitated) by caustic soda. The excess of cyanide is titrated by a standard solution of silver nitrate (Beringer's Assaying, 255). The reactions are represented by the equations:

$$4KCy+NiSO_4=K_2NiCy_4+K_2SO_4.$$
$$2KCy+AgNO_3=KAgCy_2+KNO_3.$$

Nickel and cobalt are also sometimes estimated by electrolysis, and for this purpose must be separated from zinc and other metals, dissolved in nitric acid, and precipitated in an ammoniacal solution.

Nickel is separated from cobalt by precipitation with dimethylglyoxime, and may be estimated in that way. (*See* ANALYSIS.)

Nickel in steel is precipitated by bromine water and caustic soda, after removal of the iron as basic acetate. It is weighed as NiO.

Platinum in alluvial deposits is concentrated by panning, as in the case of auriferous sands. In all cases platinum can be collected in lead by the same methods as those described under the assay of gold ores. The lead buttons are sometimes cupelled at a very high temperature, but it is difficult to remove the whole of the lead in this way, as the 'prill' freezes on the cupel when only part of the lead has been oxidised, unless a weighed amount of gold or silver is added in order to produce an alloy of lower melting point than pure platinum.

Cupellation may be finished in the oxygen-gas blowpipe flame, but the loss of platinum is then large. It is more usual to dissolve the lead button in dilute nitric acid and to filter off the platinum and gold residue, which is parted by dissolving in *aqua regia*, and precipitating the gold with oxalic acid. The platinum is estimated by difference or by precipitation as $(NH_4)_2PtCl_6$.

Platinum in alloys or in rich alluvial concentrates may be estimated by melting with six parts of pure lead, and grinding in a mortar the brittle alloy freed from slag. Portions of the alloy are scorified with fresh lead and dissolved in nitric acid.

Alloys containing gold, silver, and platinum are difficult to assay, as they are insoluble in *aqua regia*. The method adopted is first to cupel the alloy to remove copper, &c., these metals being estimated by difference. The alloy is then inquarted by cupellation with twice its weight of silver and parted by boiling in sulphuric acid. The residue contains the gold and platinum. These may be parted by again inquarting with silver and dissolving in nitric acid, provided that the amount of gold present is at least ten times that of the platinum. If the proportion of gold present is less than this, part of the platinum remains undissolved, and it is therefore necessary to add gold in many cases. The parted gold is weighed and the platinum estimated by difference (6ème Rapport des Monnaies, 1901, p. xxix.; Rose's Precious Metals, 272).

Silver. The ores of silver are assayed in the same way as those of gold of a similar kind, the scorification method being used far more frequently than in the case of gold ores. The slags and cupels must be examined usually, as silver is more readily lost than gold. The temperature of cupellation is kept as low as possible, to check the loss of silver by volatilisation (see Lodge's Notes on Assaying, 37–111).

Silver bullion and alloys are assayed by cupellation, by the Gay Lussac or the Volhard volumetric processes, or by weighing the chloride (India Mint method). In cupellation, the 'base' or oxidisable metals are removed in the muffle, and the silver prill is cleaned and weighed. The weight of silver taken is usually 10 grains. The amount of lead required varies from six times the weight of the silver for alloys of high standard to twelve times for silver 700 fine. The method is not suitable for alloys containing less than 70 p.c. of silver. The muffle is kept at a lower temperature than that required for gold cupellation, but must be raised to above the melting-point of pure silver (962°) at the finish, to prevent the metal from setting in the furnace before all the lead has been removed. When the cupellation is complete, the mouth of the furnace is closed with great care to exclude draughts, and the furnace is allowed to cool slowly to prevent loss of silver by spitting. The solidified prills are cleaned and weighed. The loss of silver in cupellation varies from 5 to 15 parts per 1000, and check assays on pure silver are placed in all parts of the furnace to measure this loss. Any gold that may be present is weighed as silver. The process is very ancient, and clear reference is made to it in connection with a trial of the Pyx in the Black Book of the Exchequer, written in the reign of Henry II.

In the Gay Lussac process, the volume is measured of a standard solution of common salt or sodium bromide required for the precipitation of a little more than a gram of silver in solution as nitrate. No indicator is used, and the end of the operation is judged from the appearance of a faint cloud of chloride in a solution from which almost all the silver has been precipitated. It is the most accurate method of assaying silver bullion. The standard solution of common salt (usually called the 'normal solution') contains about 5·416 grams of NaCl per litre, so that 100 c.c. will precipitate 1 gram of silver. A weight of silver bullion containing about 1·003 gram of silver is weighed and dissolved in nitric acid, and 100 c.c. of the salt solution added to it from a pipette. The chloride is agglomerated by a shaking in a stoppered bottle, and the clear supernatant liquid is tested by 'decinormal' solutions of common salt and, if necessary, of silver nitrate. The appearance of the cloud of silver chloride shows the amount of silver left in solution. Further shakings are resorted to if required, and the final reading is taken after waiting for about 5 or 10 minutes. Check assays on fine silver are used with every batch to test the strength of the solution, which varies with the temperature, &c. Mercury interferes with the method, and is detected by the colour of the precipitated silver chloride, which does not darken if mercury is present. Acetate of soda corrects the error if the quantity of mercury present is small. The Gay Lussac method can be used only in cases where the approximate assay is already known (Percy's Silver and Gold, 282; Riche et Forest, L'Art de l'Essayeur, 183).

In the India Mint method, the silver alloy is dissolved in nitric acid and precipitated by a slight excess of hydrochloric acid. The silver chloride is then collected by shaking in a stoppered bottle, and, after being washed, is transferred to a porous cup, dried, and weighed while warm. The chloride is washed by decantation, but the drying is tedious, and is expedited by breaking up the crust with a glass rod. Any gold that may be present is weighed as silver chloride. This is the best method for alloys containing less than 70 p.c. of silver (Trans. Inst. Mng. & Met. xvii. 334).

The Volhard method is largely used in this country. The nitric acid solution of the silver is freed from nitrous acid by boiling, and is then diluted and titrated with a solution containing 7·04 grams of ammonium thiocyanate per litre. As this salt is deliquescent, it is usual to weigh out about 7·3 grams per litre. Iron alum is used as an indicator, giving a red colour when all the silver has been precipitated. Time is saved and the accuracy of the method increased by taking for assay an amount of alloy containing about 1·003 gram of silver, and running in 100 c.c. of the standard solution of thiocyanate from a pipette. After shaking the liquid in a flask, the titration is finished by adding the thiocyanate a drop or two at a time. Check assays on fine silver are used (Trans. Inst. Mng. & Met. xvi. 154).

Tin. Tin ore is concentrated on a vanning shovel with the production of 'black tin' in order to determine what yield may be expected when the ore is treated on the dressing floors. The ore is crushed and sampled, and about 30 grams (or less with rich ores) are thoroughly mixed with 30 or 40 c.c. of water on the vanning shovel, to prevent, as far as possible, the loss of 'float tin.' The ore is then collected by a vigorous circular motion of the water, and the slimes are poured off, a process which is repeated until the water remains clear after being left to settle for a few seconds. A smaller quantity of water is used for the subsequent operations. By means of a circular motion of the shovel, combined with a series of jerks, the tin oxide is now separated from the lighter material, which is carried down by the descending wave. The tailings are sometimes saved and washed over again until they yield no more tin, and are then crushed by rubbing with a hammer and again washed. The concentrates are dried and roasted and dressed once more after being rubbed down with a hammer. Sometimes they are washed quite clean from worthless material, and sometimes left impure with oxide of iron, &c., according to the nature of the ore and the custom of the operator. Sometimes they are purified by boiling in hydrochloric acid or *aqua regia*, which, according to J. H. Collins, causes a loss of tin. The residue is usually reported in pounds of black tin to the long ton of ore. The losses of cassiterite in vanning vary considerably, and may be reckoned as 30 to 40 p.c.

The black tin obtained by vanning may be assayed for metallic tin by reduction with anthracite (Cornish method) or by fusion with potassium cyanide. In the Cornish method 100 grams of tinstone are heated with 20 grams of anthracite in a plumbago crucible at a white heat for 15 or 20 minutes before pouring. The excess of anthracite contains beads of tin, which are separated by sieving and vanning. In the cyanide process, 10 grams of tinstone are fused with 40 grams of impure cyanide (containing potassium carbonate), and poured at a red heat. The German process consists in reducing a mixture of 5 grams each of tinstone and cupric oxide with 15 grams of black flux (a mixture of carbon and potassium carbonate, obtained by heating tartar) and 1·25 grams of borax with a cover of common salt. The reduced metal is compared in weight with that of the copper reduced from cupric oxide alone. The most trustworthy of these methods is the fusion with cyanide. The reduced tin, however obtained, is usually impure (Beringer's Assaying and Kerl's Metallurgische Probirkunst).

Tin is also estimated volumetrically. A satisfactory method described by Beringer Text-Book of Assaying, 11th ed. 285) is to reduce the solution of stannic chloride to stannous chloride by means of nickel foil, and to titrate with a standard solution of iodine in an atmosphere of carbonic acid gas. Starch is used as an indicator. In all wet methods, tin oxide must be reduced to metallic tin before it can be dissolved. Beringer prefers reduction by means of zinc vapour acting on ore mixed with oxide of zinc. The alloy of zinc and tin thus produced is dissolved in hydrochloric acid, to which crystals of permanganate are added. In Pearce's method (Low's Technical Analysis. 261) the ore is fused with caustic soda and charcoal powder, and the mass dissolved in hydrochloric acid; the reduction of the stannic to stannous chloride is then effected with iron rods.

Titanium in ores is generally in the form of titanic oxide, which is insoluble in acids. Titanates, however, are somewhat soluble, so that on attacking ores with acid, titanium will be found partly in the residue and partly in the solution. The metals of the iron group with titanium are precipitated from the solution as basic acetates, which are fused with potassium bisulphate and extracted with water. The titanic acid is precipitated from the solution by means of prolonged boiling with sulphurous acid. The residue left by the attack on the original ore with acids is similarly treated, after the silica has been removed by heating with sulphuric and hydrofluoric acids (Beringer's Assaying, 293).

Tungsten in wolfram, steel, &c., is estimated by weighing as tungstic acid WO_3. The ore is boiled with hydrochloric acid followed by *aqua regia*, when the tungsten separates as insoluble yellow tungstic acid. After thorough washing, this is dissolved in ammonia, filtered, and recovered by evaporating the solution to dryness, and gently igniting the residue to decompose the ammonium tungstate. Nearly pure tungstic acid remains. Any silica that may be present may be removed by hydrofluoric acid. The tungstic acid may also be precipitated from solution by neutralising with nitric acid and adding a solution of mercurous nitrate (Beringer's Assaying, 13th ed. p. 297 d.). In attacking ores with acid, some WO_3 is dissolved in the presence of fluorides, arsenic or phosphorus, but this is corrected by the addition of cinchonine. The ores may be attacked by fusion with caustic soda and sodium peroxide, or by digesting with soda solution instead of by boiling with acid (Hutchin and Tonks, J. Inst. Mng. and Met. 18, 1909, 425).

Uranium. The mineral is evaporated with nitric acid and taken up with HCl. After separation of the other metals as sulphides and carbonates, the uranium is precipitated by ammonia and weighed as U_3O_8, or it is precipitated by microcosmic salt in the presence of acetic acid and ammonium acetate. The precipitate consists of ammonium uranyl phosphate $UO_2NH_4PO_4$ which is washed, ignited gently and weighed or converted into uranyl pyrophosphate $(UO_2)_2P_2O_7$, for greater accuracy (Low's Technical Ore Analysis, 201). This precipitation is also the basis of a volumetric method, a boiling solution of uranium being titrated with a standard solution of phosphate, until ferrocyanide no longer gives a brown colour.

Vanadium in steel is estimated by titrating with potassium permanganate. The steel is dissolved in HCl and evaporated to dryness with a little nitric acid. The residue is fused with nitre and fusion mixture, boiled in water and filtered, and the filtrate evaporated with H_2SO_4, reduced by sulphur dioxide and titrated. One atom of iron is equivalent to one of vanadium in the titration (Rhead and Sexton's Assaying, 270).

Zinc. The old dry method of assay of ores based on the loss of weight due to the volatilisation of zinc at a white heat is obsolete. Certain alloys of zinc with tin and copper, *e.g.* coinage bronze, are assayed for zinc by heating to 1200° for two hours in carbon crucibles (J. Soc. Chem. Ind. 33, 1914, 270). The loss of weight gives the zinc together with any cadmium or oxygen present. Check assays on trial plates of known composition are necessary Zinc is usually weighed as oxide after precipitation as carbonate, or it is titrated with sodium sulphide or potassium ferrocyanide. An amount of 1 or 2 grams of ore is weighed out and dissolved in hydrochloric acid or *aqua regia*. The silica and metals other than zinc are removed as usual. All the precipitates will contain zinc if they are bulky, and must be redissolved and reprecipitated. The alkaline filtrate may be diluted to 200 c.c. and used for the sodium sulphide titration, which is carried out at 50°–60°. A flake or two of freshly precipitated ferric hydrate is used as an indicator, turning from red to black as soon as sodium sulphide is in excess. One c.c. of the standard solution of sodium sulphide should be equal to 0·01 gram zinc. Instead of ferric hydrate, sodium nitroprusside may be used as an indicator on a white tile. This gives a purple colour with sodium sulphide.

For titration with potassium ferrocyanide, the pure ammoniacal solution of zinc obtained as above is acidified with hydrochloric acid, boiled and titrated hot. The standard solution of ferrocyanide is made up by dissolving 41·25 grams of the pure salt in a litre of water. The test solution consists of 0·5 gram of uranium acetate dissolved in 20 c.c. of water. A drop of this solution gives a brown colour on a white tile with a drop of the zinc solution as soon as the ferrocyanide is in excess. It is advisable to confirm the end reaction by adding 5 c.c. of a standard solution of zinc in hydrochloric acid, containing 10 grams of zinc per litre, and again titrating (Chem. News, lxxvi. 6).

The assay of zinc-dust for metallic zinc is made by acting on the sample with dilute sulphuric acid, and collecting and measuring the hydrogen which is evolved.

Commercial metallic zinc contains lead, cadmium, and iron, and may also contain arsenic, copper, antimony, tin, &c. By dissolving in dilute sulphuric acid, the lead and the greater part of the copper, tin, cadmium, &c., are left undissolved. The residue is attacked with nitric acid, and the metals separated as usual. Iron in zinc is titrated in the sulphuric acid solution without being separated. Arsenic and antimony are passed with the hydrogen evolved by sulphuric acid into a solution of silver nitrate (Campredon, Guide Pratique, 760; Eliot and Storer, Amer. Acad. Arts & Sciences, viii. 57).

Coal. The assay of coal usually comprises the determination of moisture, total ash, sulphur, coking properties, and calorific power. The coal is broken down and sampled as in the case of ores (see p. 408), and the sample is passed through an 80-mesh sieve.

The moisture is determined by drying 1 gram in a water-oven for 30 minutes and weighing. The coal is then again warmed for 15 minutes and reweighed, and the process is continued until the weight is constant or begins to increase.

For sulphur, 2 grams of coal are mixed with 3 grams of a mixture of two parts of calcined magnesia and one part of potassium carbonate, and heated to dull redness for an hour in a porcelain or platinum crucible, with occasional stirring. After cooling, the charge is transferred to a beaker and digested with water and 1 c.c. of bromine. It is then acidulated with hydrochloric acid, the bromine boiled off, and the sulphur, now in the form of sulphate, precipitated by barium chloride. The sulphur may also be oxidised by heating the coal with a mixture of nitre and common salt. Phosphorus in coal, if determined at all, is estimated in the ash, which may require complete analysis.

The coking qualities of coal are examined by heating 50 grams of coarsely crushed coal in a 'large copper' crucible covered with a closely fitting lid. The evolution of gases is completed after 15 or 20 minutes at a full red heat. After cooling, the coke is turned out and weighed, the loss of weight giving the amount of volatile matter.

The calorific power of coal is determined by igniting 2 grams of the finely powdered sample with 20 grams of a mixture of six parts of potassium chlorate and one part of nitre. The coal and deflagrating mixture are ground together in a mortar and ignited in a Thompson calorimeter. The error due to loss of heat by escaping gases, &c., is always taken as one-tenth of the total evolved. The calorific power reported is the weight of water that could be evaporated at 100° and 760 mm. pressure by a unit weight of the fuel (*v.* FUEL).

Cyanide solutions. In gold mills, these solutions are in wide use, and require frequent analysis. Free cyanide is estimated by means of a solution of silver nitrate prepared by dissolving 13·04 grams of crystallised $AgNO_3$ in a litre of water. One c.c. of this solution is equivalent to 0·01 gram of KCy, the end of the titration being denoted by the solution becoming milky from the precipitation of AgCy. The reaction is represented by the equation:

$$AgNO_3+2KCy=KAgCy_2+KNO_3.$$

The amount of cyanide solution taken for assay may be from 10 c.c. to 100 c.c., according to its strength. Alkalis and other compounds which may be present dissolve silver cyanide, and accordingly it is usual to add potassium iodide as an indicator. Turbid cyanide solution must be filtered before titration. If soluble sulphides are present, they prevent the assay from being carried out. They are removed by agitating the solution with freshly precipitated lead carbonate. If zinc is present in the solution, part of the cyanide contained in the double cyanide K_2ZnCy_4 is estimated as free KCy.

The 'total alkali' in a cyanide solution is estimated (J. E. Clennell, Chemistry of Cyanide Solutions, 62) by titration with a standard solution of sulphuric acid, using methyl orange as an indicator. 'Protective alkali' (*op. cit.* 63) is determined by adding a slight excess of silver nitrate together with a little phenolphthalein solution, and titrating with sulphuric acid until the pink colour disappears. The 'reducing power' of cyanide solutions is determined by acidification and subsequent titration with potassium permanganate, until the pink tint becomes permanent, or by adding an excess of permanganate followed by an excess of potassium iodide and estimating the amount of iodine liberated (*op. cit.* 71).

Gold and silver in cyanide solutions are determined by evaporation on lead foil, which is afterwards cupelled, or by evaporation with litharge, which is fused for lead. A more rapid method is to precipitate the gold and silver with zinc-dust and sulphuric acid, filter, and scorify or fuse the residue. The latter method is especially suitable for treating large samples of poor solutions containing very little gold and silver. In all these methods, a button of lead is obtained which is cupelled and the gold and silver parted as usual.

Silica. The silica in ores is partly free and partly combined. The white sandy residue left after careful extraction with acids is sometimes nearly pure silica, and is often reported as 'silica and silicates insoluble in acids.' It may be tested with sulphuric and hydrofluoric acids. The usual method with ores, slags, &c., is to fuse 1 gram with 5 grams of fusion mixture and a little nitre in a platinum crucible or dish. It is extracted with warm water and a little hydrochloric acid and evaporated to dryness on a water-bath. The bases are dissolved out with hydrochloric acid, and the silica filtered off. The filtrate is again taken to dryness and dissolved in hydrochloric acid to separate the remainder of the silica. If the ore contains a large percentage of sulphides, oxides, &c., which are soluble in acids, these are removed before the fusion. In this case the acid solution may contain silica, which is removed by evaporating to dryness, taking up with hydrochloric acid and filtering. The purity of the silica is tested by evaporating two or three times with water, sulphuric acid and hydrofluoric acid. The silica is volatilised (J. Amer. Chem. Soc. xxiv. 1902, 362).

Sulphur. A rapid method of determining the sulphur in ores given by Furman (Manual of Practical Assaying, 5th ed. 91) is to fuse 5 grams of the ore with 15 grams of borax, 3 grams of charcoal, and one or two nails in a hot fire. The time required for fusion is about 15 minutes. The nails are then withdrawn and the charge poured. As soon as the slag is cool, the matte is detached from it with a hammer and weighed. If the matte were pure FeS, it would contain 36·3 p.c. of sulphur. By analysis, Furman finds that the nearest approximation is to take the sulphur as 30 p.c. of the matte. The method, though inaccurate, is sometimes useful, as it can be completed in less than half an hour.

The more accurate methods consist in oxidising the sulphur by *aqua regia* or nitric acid and potassium chlorate, or by fusion with a mixture of nitre and sodium carbonate, and weighing it as barium sulphate. A good method for ores and slags consists in fusion with caustic alkali, extracting with water, and oxidising with bromine. After separation of the silica, the sulphur is precipitated by barium chloride (Chem. News, l. 1884, 194). If lead is present, the solution is boiled with ammonium carbonate.

T. K. R.

ASTATKI. A Russian term, signifying 'dregs,' applied to the residue left in the distillation of Baku petroleum after the volatilisation of the kerosene, and now largely used as fuel in the Caspian region (*v.* PETROLEUM).

ASTERIA (*Star Sapphire*) *v.* CORUNDUM.

ASTERIN *v.* ANTHOCYANINS.

ASTEROL. A combination of the mercury salt of *p*-phenol-sulphonic acid (hydragyrol) and ammonium tartrate

$$C_{12}H_{10}O_8S_2Hg,4[C_4H_4O_6(NH_4)_2],8H_2O,$$

used as an antiseptic in surgery.

ASTRALINE. Russian petroleum oil, used for burning (*v.* PETROLEUM).

ASTRALITE. A glass resembling aventurine, but containing crystals of a cupreous compound which by reflected light exhibit a dichroic iridescence of dark red and greenish-blue. Made by fusing and allowing to cool slowly a mixture of 80 pts. silica, 120 lead oxide, 72 sodium carbonate, 18 borax, with either 24 pts. scale oxide of copper, and 1 pt. scale oxide of iron, or with 5 pts. lime, 26 copper oxide, and 2 iron oxide.

ASTROLIN. Trade name for antipyrine-methyl-ethyl glycollate $C_5H_{10}O_3,C_{11}H_{12}ON_2$, m.p. 64°–65·5°. A colourless powder, with a slight smell and pleasant taste, readily soluble in water and alcohol.

ASUROL. Sodium-mercuri-amido-oxy*iso*-butyrosalicylate.

ASYPHIL. Trade name for a *mercury salt of p-aminophenylarsinic acid*

$$(NH_2C_6H_4AsO(OH)O)_2Hg$$

(*v.* ARSENICALS, ORGANIC).

ATACAMITE. Hydrated oxychloride of copper $CuCl_2{\cdot}3Cu(OH)_2$, occurring in the Atacama region of Chile, sometimes in sufficient amounts for use as a copper ore (Cu 59·4 p.c.). Large quantities have also been mined at Wallaroo in South Australia. Orthorhombic crystals of a bright-green colour and with brilliant faces are not uncommon. Sp.gr. 3·76. Before the days of blotting-paper, it was used, under the name of arsenillo, as a writing sand for absorbing ink (*v.* COPPER).

L. J. S.

ATELESITE. A bismuth arsenate containing iron phosphate found at Schneeberg in Saxony: Bi_2O_3, 57·15; $Fe_2P_2O_8$, 12·50; As_2O_3, 30·35 (Frenzel, J. M. 1873, 785).

ATHAR or **ATTAR**, Indian name for volatile oil of roses (*v.* OILS, ESSENTIAL).

ATISINE, *v.* ACONITINE

ATLAS DYNAMITE *v.* EXPLOSIVES.

ATLAS POWDER *v.* EXPLOSIVES.

ATLAS SCARLET *v.* AZO- COLOURING MATTERS.

ATMOSPHERE. The gaseous envelope surrounding any liquid or solid body; more particularly the gaseous envelope which surrounds the earth, and which is commonly known as air. The thickness of this aërial envelope is not known even approximately, but it is quite certain that it exceeds 45 miles measured from the earth's surface, which was the limit assigned to it by Wollaston. Secchi calculated that air exists even at a height of 300 kilometres above the earth's surface. From the ratio of decrease of density with elevation, the atmosphere at a height of 50 miles cannot exert any measurable pressure. The mass of the atmosphere forms, like the earth itself, an oblate spheroid, the polar axis of which is much shorter than the equatorial axis, the ratio of the two axes being, according to Laplace, as 2 to 3.

The pressure of the atmosphere at any particular spot may be measured in terms of the height of a column of mercury which it is capable of sustaining. It follows from the law of Boyle that the density of the air rapidly diminishes with the height. For air of constant temperature, its density, or, what comes to the same thing, the height of the mercurial column, should diminish in geometric progression, whilst the distance from the earth increases in arithmetic progression. The pressure, even at the same place, is continually varying from a variety of causes, and hence the height of the barometer, as the mercurial column was first termed by Boyle, is practically never absolutely constant. The average height at any one spot at the sea-level is mainly dependent upon the great movements of air which result from the effect of the earth's motion upon the gaseous envelope, combined with variations in the density of the aerial mass due to solar action.

According to Regnault, 1 litre of dry air, free from carbonic acid and ammonia, measured at 0° and 0·76 mm. pressure, at Paris (lat. 48° 50′) and at a height of 60 metres above the sea-level, weighs 1·293187 grams. Lasch found that 1 litre of pure air at standard temperature and pressure weighs at Berlin (lat. 52° 36′) 1·293635 grams.

Guye found 1·2930 grams at Geneva, and concluded that it may vary, on the same day, from place to place to the extent of several tenths of a milligram (Guye, Kovacs and Wourtzel, Compt. rend. 1912, 154, 1584). The mean of the most recent determinations gives the value 1·2928 grams as the weight of a normal litre of air. Guye considers that the most probable explanation of the variations in density observed from time to time is based on the presence in the air of varying quantities of dust, invisible under the ultramicroscope.

The Bureau Internat. des Poids et Mesures adopts for the weight of 1 litre of dry air, containing 0·04 p.c. carbonic acid, at the normal temperature, and under the normal barometric pressure at lat. 45° and sea-level,

$$P_{t,t}=\frac{1{\cdot}293052}{1+0{\cdot}00367}\times\frac{1}{760},$$

on the assumption that 0·00367 is the expansion coefficient of air at constant pressure for a normal degree. According to Leduc the mean composition of air at Paris, purified from aqueous vapour and gases absorbable by alkali, is as follows:

	Oxygen	Nitrogen	Argon	Neon
By volume	0·2100	0·7806	0·0094	15×10^{-6}
By weight	0·2321	0·7549	0·0130	$8{\cdot}4\times10^{-6}$

	Helium	Hydrogen	Krypton	Xenon
By volume	$0{\cdot}5\times10^{-6}$	1×10^{-6}	50×10^{-9}	6×10^{-9}
By weight	$0{\cdot}7\times10^{-6}$	$0{\cdot}07\times10^{-6}$	140×10^{-9}	30×10^{-9}

For such air at 0° and a pressure of 76 cm. of mercury at Paris the mass of 1 litre is found to be 1·2932 grm. Under normal pressure (76 cm. of mercury at 0°; $g=980{\cdot}665$) the weight is 1·2928. In other terms, taking the sp.gr. of mercury as 13·5951 and the value of g at the 4th story of the Sorbonne as 980·97, the mass of a litre of air under the pressure of a megabar is 1·2759 grm. For purposes of ordinary chemical calculation it may be assumed with sufficient accuracy that 1 gram of air measures at standard temperature and pressure 773 c.c.

The total weight of the atmosphere is about 11 trillions of pounds, or about 5 trillion kilograms and the relative amounts of the chief constituents may be assumed to be—

	Trillions kgm.
Nitrogen (argon, &c.) .	4·041200
Oxygen	1·218040
Carbonic acid . .	0·003156
	5·262396

Herschel calculated that, allowing for the space occupied by the land above the sea, the mass of the atmosphere is about $\frac{1}{1200000}$ part of that of the earth.

The unit of pressure adopted by engineers and others, and styled an *atmosphere*, is an amount equal to the average pressure of the atmosphere at the sea's level. In British measure an atmosphere is the pressure equivalent to 29·905 inches of mercury at 32° F. at London, and is about 14·73 lbs. on the sq. inch. In the metric system it is the pressure of 760 mm. (29·922 inches) at 0° C. at Paris, and is equal to 1·033 kilos on a sq. centimetre. Hence the English 'atmosphere' is 0·99968 that of the metric system.

The specific heat of air at constant pressure is 0·239 (Hercus and Laby). Its coefficient of thermal expansion between −30° and 200° is 0·003665 for 1°. Its thermal conductivity is $5{\cdot}22\times10^{-5}$ cal./cm. sec. deg. (Hercus and Laby, Proc. Roy. Soc. 1918, A, 206). Its viscosity $(N_0\times10^4)=1{\cdot}733$.

By the application of sufficient cold and pressure, air may be liquefied.

Comparatively little of the sun's heat is absorbed in its direct passage through the air. According to Tyndall, a column of air 1 metre long absorbs 0·088 p.c. of the heat which passes through it. According to Violle, and also Lecher and Pernter, the amount is not greater than 0·0070 p.c. This absorption is mainly due to aqueous vapour, and, in a lower degree, to carbonic acid and suspended organic matter. The air mainly gets its heat by conduction from the earth, and hence, as a rule, it is hottest near the ground. The law of the decrement in temperature corresponding to height is not accurately known; it is usually stated to be about 0·56° per 100 metres, but the rate is liable to very great variations.

Air is not perfectly transparent. Its particles reflect and scatter light in sufficient quantity to obscure the light from the stars. The blue colour of the sky is due to the fact that the most refrangible rays are most widely scattered (*cf* Rayleigh, Phil. Mag. 1899, 47, 375). Strutt has devised a method of showing the scattering of light by dust-free air and of artificially reproducing the blue colour of the sky (Proc. Roy. Soc. 1918, 94 A, 453; *see* also Cabannes, Compt. rend. 1915, 160, 62). In the higher regions of the atmosphere, where the amount of reflected light becomes less and less, owing to the decreased density of the air, the sky appears to grow gradually darker. Brewster first proved that the blue light from the sky, as well as the white light from the clouds, was due to reflected light, by the fact that it was polarised.

Suspended matter, dust, smoke, aqueous vapour in a state of partial precipitation, &c., greatly diminish the transparency of air. Wild gives the following numbers as representing the transparency coefficient of 1 metre of air:—

Dry air (free from dust) . . . 0·99718
Air of a room (dry, but containing dust) . . . . 0·99520
Air free from dust, but saturated with aqueous vapour . . . . 0·99328

The refractive indices of dry air at standard temperature and pressure for the Fraunhofer lines A, B, C, D, E, F, G, H, are, according to Kettler (Pogg. Ann. 124–401), as follows:—

$nA = 1{\cdot}00029286$
$nB = 1{\cdot}00029345$
$nC = 1{\cdot}00029383$
$nD = 1{\cdot}00029470$
$nE = 1{\cdot}00029584$
$nF = 1{\cdot}00029685$
$nG = 1{\cdot}00029873$
$nH = 1{\cdot}00030026$

The emission spectrum of air has been mapped by Huggins (Phil. Trans. 154, 139) and Angstrom (Pogg. Ann. 94, 141), and the spectrum of lightning by Kundt (Pogg. Ann 135, 315), who has shown that forked lightning gives a line spectrum, whereas sheet lightning gives a band spectrum. The absorption spectrum of air was first mapped by Brewster and Gladstone, and has been further examined by Janssen, Cornu, and Chappuis (Compt. rend. 91, 988).

Air, owing to the oxygen it contains, is a magnetic substance. The diurnal variation in magnetic declination has been alleged to be due to the varying magnetic potential of the oxygen owing to alterations in temperature

Air is a mixture of nitrogen, oxygen, aqueous vapour, argon, carbon dioxide, with minute quantities of ozone, hydrogen peroxide, ammonia, nitrous and nitric acids, hydrocarbons, helium, neon, krypton, xenon, hydrogen, &c. That the air is not a chemical compound of its component gases is proved by the facts: (1) that these gases are not present in any constant ratio; (2) that air can be made by simply mixing its constituents in the proportion indicated by the analysis of air, without contraction or any thermal disturbance resulting; (3) that on treating air with water and expelling the dissolved air by boiling, the proportion of the oxygen to the nitrogen is found to be increased, and in amount corresponding with the law of partial pressures; (4) that the constituents of the air can be mechanically separated by processes of diffusion; and (5) that the refractive power of the air is equal to the mean of the refractive powers of its constituents, whereas in compound gases the refractive power is either greater or less than the refractive power of the elements in a state of mixture.

The amount of **oxygen** in air may be ascertained by measuring the diminution in volume which a known bulk experiences when in contact with some substance capable of absorbing or combining with oxygen gas. Among the substances which may be conveniently used for this purpose are:

1. *Phosphorus.* A fragment of phosphorus on the end of a platinum or copper wire is exposed to a measured volume of air standing over water or mercury until no further decrease of volu[illegible]ed (Berthollet) Lindemann (Zeitsch anal Chem 1879, 18, 158) employs thin sticks of phosphorus for the same purpose in the Orsat apparatus (*v.* GAS ANALYSIS). At a temperature below 7° the oxidation of the phosphorus ceases. Watson (Chem. Soc. Trans. 1911, 99, 1460) has described an accurate method of ascertaining the amount of oxygen in air by the use of yellow phosphorus. A modification of the apparatus for estimating the oxygen content of air from the upper atmosphere has been suggested by Aston (Chem. Soc. Trans. 1919, 472).

2 *Pyrogallol in Alkaline solution.* Chevreul, in 1820, first suggested the use of this reagent. The absorption is apt to be accompanied by the formation of notable quantities of carbon monoxide if the amount of oxygen is large or the alkaline solution very concentrated. According to Hempel (Ber. 20, 1865), the best proportions are 5 grams pyrogallol dissolved in 15 c.c. water mixed with 120 grams caustic potash dissolved in 80 cm. of water. Practically no carbon monoxide is formed with this solution. The absorption is very rapid (Hempel, Ber. 18, 267 and 1800). Guye and Germann have described a volumeter by which it is possible to analyse accurately very small quantities of air (0·25 c.c.) (Compt. rend. 1914, 159, 154).

3. *Metallic Copper.* A spiral of copper wire is heated to redness in dry air free from carbonic acid and of known pressure until the whole of the oxygen has combined with the metal to form cupric oxide. The pressure of the residual gas is then determined, whereby the amount of nitrogen is ascertained, and hence the amount of oxygen. An apparatus on this principle was suggested by Jolly (W. N. S. 6538); it is seen in Fig. 1.

The glass vessel A, of about 100 c.c. capacity, is exhausted by the mercurial pump, and is replenished with the air under investigation. This is then cooled to 0 by surrounding A

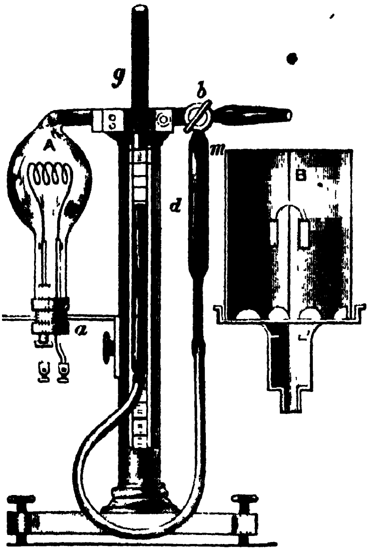


Fig 1

with the metallic cylinder B, which is filled with melting ice. The tension of the confined air is measured by the height of mercury in the glass tubes *g* and *d*, which are connected together by caoutchouc tubing. The tube *g* is movable in the clamp *f*, the position of *d* being fixed with reference to A. By turning the three-way stop-cock *b*, A and *d* may be alone brought into connection, or both may be made to connect with the outer atmosphere. The cock is now so turned that A and *d* are alone in connection; the tube *g* is now raised until the level of the mercury in *d* just touches the point *m*, when the tension of the air is read off on the graduated scale behind *g*. The copper spiral in A is next heated to redness by an electric current, whereby the heated metal rapidly combines with the oxygen. The cylinder B is once more placed round A, the residual nitrogen cooled down to 0° by means of melting ice, and its tension measured by adjusting the level of the mercury to *m*, and reading off the height of the mercury in *g*. If, for example, the pressure before abstracting the oxygen was 702·56 mm., and after the abstraction was 555·70 mm., then 1 volume of the air would be reduced to $=\frac{555\cdot70}{702\cdot56}=0\cdot79096$ vol., or, expressed centesimally, the composition of the air would be:

Nitrogen (argon, &c.) . . .	79·096
Oxygen	20·904
	100·000

Kreusler has shown that unless the air be carefully dried before being heated with the copper spiral, the proportion of oxygen will be apparently too low.

Dumas and Boussingault (Ann. Chim. Phys. [3] 3257), as far back as 1841, made use of the fact that heated metallic copper combines with oxygen, in order to determine the gravimetric composition of air. Air deprived of moisture and carbonic acid was passed through a weighed tube containing metallic copper heated to redness, whereby all the oxygen was absorbed, the nitrogen being collected in a vacuous glass globe also previously weighed. At the conclusion of the experiment the tube containing the metallic copper was again weighed; the increase in its weight gave the amount of absorbed oxygen, together with the weight of the nitrogen which it also contained. The nitrogen was then removed by the air pump and the tube again weighed; the difference between the first and third weighings of the tube containing the copper gave the weight of absorbed oxygen, and the weight of nitrogen was obtained by adding the difference between the second and third weighings of the tube to the increase in the weight of the glass globe. As the mean of a large number of experiments made by this method, the precentage composition by weight of air free from water and carbonic acid was found to be

Oxygen	23·00
Nitrogen (with argon, &c.) .	77·00
	100·00

Leduc has shown that this proportion of oxygen is too low, as an average; the amount is about 23·2 p.c. by weight as calculated from the known density of air and of its constituent gases (Compt. rend. 1896, 12, 1805; 1898, 126, 413).

4. *Explosion with hydrogen.* A measured volume of air is mixed with a known volume of hydrogen in excess, and the mixture is exploded by the electric spark, when the oxygen combines with the hydrogen in the proportion of 1 vol. of the former to 2 of the latter to form water. One-third of the contraction resulting from the explosion represents, therefore, the amount of oxygen in the air under examination. This method, first suggested by Volta, was perfected by Bunsen. Modifications of the method have been made by Regnault and Reiset, Williamson and Russell, Frankland and Ward, and others. These methods are extremely accurate, and have afforded us all the exact knowledge we have respecting the variations in the amount of oxygen in atmospheric air. Thus Bunsen, in a series of analyses made in the winter of 1846, found that the percentage amount varied from 20·97 to 20·84. Regnault made a large number of analyses of air collected from all parts of the world. In 100 analyses of air collected in Paris the minimum amount of oxygen was 20·913, the maximum 20·999. Air collected in various parts of Europe, from above the Atlantic Ocean, from the summits of the Andes and from the South Polar Sea, contained an amount of oxygen varying from 20·86 to 21 p.c. Many hundreds of analyses were made by Angus Smith, of air collected in various towns in England and Scotland, and also of air collected in the country. The oxygen in London air varied from 20·857 to 20·95, less oxygen as a rule being found in the air of streets than in that of the parks and open spaces. A series of 30 analyses of Glasgow air showed variations from 20·887 in the closer parts to 20·929 in the more open spaces. Even wider extremes were found by Leeds in the air of New York, viz. from 20·821 to 21·029 p.c. According to E. W. Morley, the diminished proportion of oxygen may be caused by the down-rush of air from the higher regions of the atmosphere, which probably contain a less relative amount of oxygen. Regnault's experiments afford some evidence for the belief that the air of the tropics contains slightly less oxygen than that in northern latitudes (*v.* also Jolly, W. N. F. 61, 520). A similar conclusion has been drawn by Hempel (Ber. 20, 1864) from the analysis of a large number of analyses of air collected simultaneously at Tromsö, Dresden, and Para. The mean results were:

	Oxygen.
Tromsö	20·92
Dresden	20·90
Para	20·89

From the results of 203 analyses of air collected at five different spots and analysed by three independent methods, it follows that the most probable mean percentage amount of oxygen is 20·95. Numerous determinations by Pettersson and Högland of the air of Stockholm during October, November, and December, 1889, gave O=20·94 (Ber. 22, 3324; Hempel, Ber. 20, 1864; Kreusler, Ber. 20, 991). More recent work by Durius and Zuntz, Watson (Chem. Soc. Trans. 1911, 99, 1460), and Benedict (Carnegie Inst. Report, 166), indicates that such small variations as occur are not traceable to meteorological conditions. The mean percentage of oxygen (20·952) found by Benedict from 1909 to 1912 corresponds closely with that found by Morley (20·955) in 1881.

Air from various parts of France, the Alps, and Algiers, taken both in spring and winter, was found by Leduc to show on an average 23·20–23·21 p,c. of oxygen by weight, the extreme values being 23·05 and 23·25 p.c. The percentage is slightly lower in the north and at sea-level than elsewhere, and is less in London than in Paris. Samples of the upper air are less rich in oxygen than air at the level of the earth, although the differences are much less than are indicated by the law of Laplace.

Ozone is always present in minute quantity in normal air. Air over marshes contains little or no ozone. No ozone can be detected in the air of large towns or in inhabited houses. Atmospheric ozone is probably formed by the action of electricity on air. Most of the information we at present possess concerning the distribution of atmospheric ozone has been obtained by the use of so-called ozone papers. Of these the best known is Schönbein's, which is based on the fact that ozone liberates iodine from potassium iodide, and thereby renders starch blue. To prepare them, unsized paper is immersed in a solution of 15 parts starch and 1 part potassium iodide in 200 parts of water and dried in the dark. To make a determination of ozone the paper is freely exposed to the air for some hours and moistened with water, and the depth of tint produced compared with a standard scale of colour. The method has no pretensions to scientific accuracy. Houzeau (Ann. Chim. Phys. 4, 27, 5) determines the relative amount of ozone by exposing red litmus paper previously dipped in 1 p.c. sol. of potassium iodide and dried, to the action of the air. The ozone liberates iodine and the free alkali turns the paper blue. Thallium salts are turned brown by the action of ozone, and hence papers soaked in solution of these salts have been used for the recognition of ozone. Paper soaked in a very dilute solution of neutral gold chloride is turned a deep violet colour by ozone (Böttger, Chim. Zentr. 1880, 719).

Attempts have been made to estimate ozone by aspirating large volumes of air through dilute solutions of hydriodic acid and determining the amount of the liberated iodine by iodometric analysis. Also by leading the air through a mixed solution of potassium arsenite and potassium iodide, whereby the liberated iodine converts the arsenite to arsenate. The liquid through which the air had passed was then mixed with a few drops of ammonium carbonate solution and starch paste, and a standard solution of iodine (1 : 1000) added until the blue colour was permanent. A precisely similar experiment was made on equal amounts of distilled water, iodine, arsenite, &c., used, and from the difference in the amount of iodine solution needed the amount of oxidised arsenite and hence the quantity of ozone was determined.

According to David (Compt. rend. 1917, 164, 430) the ozone in air may be estimated by adding 5 c.c. of $N/100$-ferrous ammonium sulphate acidified with sulphuric acid to a vessel of 1 litre capacity, and then titrating back with $N/1000$ potassium permanganate.

Pring (Proc. Roy. Soc. 1914, A 90, 204), by observations on the action of ozone on aqueous solutions of potassium iodide, with the formation of hypoiodite and free iodine, finds that the average amount of ozone in the atmosphere is 2·5 vols. per million of air, and that this amount varies very little with the altitude between 5 and 20 kilometres. In the Alps a mean value of 2·5 vols. was observed at 2100 metres, and 4·7 vols. at 3580 metres. Pring regards ozone as a contributing factor in determining the blue colour of the sky. The use of potassium iodide as an agent for the estimation of atmospheric ozone is deprecated by Usher and Rao (Chem. Soc. Trans. 1917, 111, 799), who have devised a method in which the air to be examined is shaken with a dilute standard solution of sodium nitrite made slightly alkaline; and the unchanged nitrite content subsequently determined colorimetrically by the production of the red dye with α-naphthylamine and sulphanilic acid (Griess-Ilosvay method). For particulars the original description must be consulted.

It appears that the amount of ozone varies with the seasons: it is greatest in winter, becomes gradually less during spring and autumn, and is least in summer. Ozone is more frequently observed on rainy days than in fine weather; thunderstorms, gales, and hurricanes are frequently accompanied by relatively strong manifestations of it (*cf.* Thierry, Compt. rend. 1897, 124, 460).

According to Holmes (Amer. Chem. J. 1912, 47, 497) the maximum amount of ozone in the air is only found when 'high' barometric areas are so near that the air from great heights flows rapidly down to the earth. Most of the ozone is produced by the action of the sun's ultraviolet rays on the upper air (*cf.* Strutt, Proc. Roy. Soc. 1917, 94, 260). According to Moore (Proc. Roy. Soc. 1918, B, 90, 158), the 'ozone' odour in air is probably due to oxides of nitrogen formed by the action of sunlight rich in ultraviolet light in the upper layers of the atmosphere on air and water-vapour.

It is highly probable that many so-called ozone manifestations are due to the existence of *hydrogen peroxide* in the air, which was first demonstrated by Meissner in 1863. Schöne found from observations made at Moscow, that it was invariably present in rain, dew, and snow, and was less in winter than in summer; and more in southerly winds than in those from the north. The amounts in all cases were, however, very minute, the maximum being 1·4 c.c., and the mean 0·38 c.c. hydrogen peroxide vapour in 1000 c.c. air.

The quantity of *aqueous vapour* in the air varies with the temperature: thus 1 cm. of air when saturated with water contains:

At −10°	2·284 grams	At +20°	17·157 grams
0°	4·871 „	25°	22·843 „
+ 5°	6·795 „	30°	30·095 „
10°	9·362 „	35°	39·252 „
15°	12·746 „		

The most accurate method of determining the amount of aqueous vapour in the air consists in aspirating a given volume of the air through weighed tubes filled with some hygroscopic substance, such as phosphoric oxide or pumice soaked in oil of vitriol and reweighing the tubes, when the increase of weight gives the quantity of moisture present.

Usually, however, the humidity of the air is estimated by means of hygrometers, the best-known form of which is the psychrometer or wet-and-dry-bulb thermometer of August. The *absolute humidity* of the air is the weight of aqueous vapour contained in 1 c.m. The *relative humidity* denotes the relation between the weight actually present and that which could be theoretically present if the air were saturated; it is usually expressed in per cent. of the maximum humidity. The air is seldom absolutely saturated with aqueous vapour, although in our moist climate saturation is occasionally very nearly attained. With us the most humid month is December, and the driest is July.

The presence of *carbonic acid* in the atmosphere was first indicated by Black in 1752. The quantity in normal air is about 0·03 p.c.; in that of large towns it is slightly greater. Angus Smith gives the following summary of results obtained in London in 1864 and 1869 (Air and Rain, 53–58):—

Over River Thames .	8 expts.	0·0343 p.c.
In the Park . .	5 ,,	0·0301 ,,
In the streets . .	10 ,,	0·0380 ,,

Any circumstance which interferes with the ready diffusion of the products of respiration and of the combustion of fuel will tend to increase the relative amount of carbonic acid in the air of a town: hence during fogs the amount may be as great as 0·1 p.c.

The amount of carbonic acid in the air of the country at night is usually greater than in the day, as the following comparison shows:—

Air in the day-time.

Observer	Year	Place	Amount
Fr. Schulze .	1861–71	Rostock .	0·0292 p.c.
T. Reiset . .	1873–80	Ecorchebœuf	0·0290 ,,
G. F. Armstrong	1879	Grasmere .	0·0296 ,,
Müntz & Aubin .	1881	Vincennes .	0·0284 ,,
A. Levy . .	1877–83	Montsouris .	0·0299 ,,
Petermann .	1892	Gembloux .	0·0299 ,,
Brown & Escombe	1898–1901	Kew . .	0·0294 ,,
Air in the night-time.			
T. Reiset . .	1873–80	Ecorchebœuf	0·0304 p.c.
G. F. Armstrong	1879	Grasmere .	0·0330 ,,

These differences are mainly due to the exhalation of carbonic acid from plants at night, and, to a smaller extent, to the absence of wind and of any decomposition of the gas by the action of sunlight. Over the sea this diurnal variation is not perceived, as the following results indicate:—

Carbonic acid in sea air.

T. E. Thorpe	Irish Channel and Atlantic Ocean	1865–6	Day .	0·0301 p.c.
			Night	0·0299 ,,
			Mean 0·0300	

In cold regions the dissociation pressure of hydrogen carbonates in the sea being low, the proportion of carbon dioxide in the air is below normal. Samples of air collected over the sea at latitudes of 64–70, at temperatures between 1° and 2°, gave a mean value of 2·0524 vols. in 10,000 of air, a distinctly smaller proportion than is met with in warmer regions (Muntz and Lainé, Compt. rend. 1911, 153, 1116).

Carbonic acid in the air of tropical countries.

T. E. Thorpe . .	S. America .	1866	0·0328 p.c.
Müntz & Aubin .	S. and Central America .	1882	0·0278 ,,
		Mean 0·0303	

The pressure exerted by the carbonic acid in air is so small that its amount is not perceptibly diminished by rain. The amount also is not sensibly altered in the higher regions of the atmosphere.

Of the several methods which have been proposed for the estimation of atmospheric carbonic acid, the most generally convenient is that of Pettenkofer. It consists in exposing a known volume (say 50 c.c.) of dilute baryta water of known strength to a measured quantity of air (4–6 litres) contained in a well-closed flask. In about 5 or 6 hours the absorption of the carbonic acid will be complete, provided that the sides of the flask have been moistened from time to time by the baryta solution. The baryta solution is then decanted and allowed to stand in a small stoppered bottle until the barium carbonate has settled, when aliquot portions (say 20 c.c.) of the clear solution are withdrawn and the amount of the baryta still in solution determined by titration with a standard solution of sulphuric or hydrochloric acid, of which 1 c.c. = 1 mgm. CO_2, phenolthalein being used as indicator (*v.* ACIDIMETRY). The difference in the volume of acid needed for the neutralisation of the baryta before and after exposure to the confined volume of air gives the number of milligrams of carbonic acid contained in the air. Blochmann (Annalen, 237, 72) has described a modification of the apparatus which allows of the titration being effected without exposure to the air of the laboratory.

(For other methods, *v.* Haldane and Pembrey, Roy. Soc. Proc. 1889; Cl. Winkler, Chem. Unter. der Industriegase, Freiberg, 1877; Reiset, Chem. Soc. Trans. 90, 1144; Müntz and Aubin, Compt. rend. 92, 247.)

(For Angus Smith's minimetric method, *v.* Air and Rain; compare Lunge, Dingl. poly. J. 231, 331.)

(On the influence of the sea upon the amount of atmospheric carbonic acid, *v.* Levy, Ann. Chim. Phys. [3] 34, 5; Thorpe, Chem. Soc. Trans. 1867; Schloesing, Compt. rend. 93, 1410; Lawes, Phil Mag. [5] 11, 206.)

Minute quantities of ammonia and nitrous and nitric acids are also present in the air. Although many of the published observations are probably inaccurate owing to the imperfection of the methods employed, it appears to be proved that the amount of ammonia, which exists mainly as carbonate, is subject to very great variations. By aspirating from 10 to 20 litres of air through Nessler's solution (an alkaline solution of potassium-mercury iodide) and comparing the depth of colour with that produced by a standard solution of an ammonium salt, H. T. Brown (Roy. Soc. Proc. 18, 286) found that the air of Burton-on-Trent during September, October, and November, 1869, taken 2 metres from the ground, contained from 0·4059 to 0·8732 part $(NH_4)_2CO_3$ in 100,000 parts of air, whereas that of the country taken during December and February contained from 0·5102 to 0·6085 part. The direction of the wind had apparently no influence on the amount; heavy rain seemed to diminish it, but the air was restored to its normal condition in a few hours. Truchot found from 0·93 to 2·79 mgm. per cubic metre in the air of Auvergne, the minimum being found in clear weather and the maximum during fogs (Compt. rend. 77, 1059). Müntz and Aubin, from observations on rain water, found that the upper strata of air contain much less ammonia than air near the ground. Levy (Compt. rend. 91, 94) found that the rain water and snow of Paris contain in mean 1·17 mgm. of ammoniacal nitrogen per litre of water. The amount of ammonia in this meteoric water is least in winter and greatest during the warmer periods of the year. Gilbert and Lawes found that 1,000,000 pts. of rain water collected in the country contained 0·927 to 1·142 pts. of ammonia. Rain water collected in towns always contains large quantities of ammonia. Thus Angus Smith found that rain water collected in the sparsely populated districts in Scotland contained 0·53 pt. per million, whereas the rain water of London contained 3·45, that of Liverpool 5·38, that of Manchester 6·47, and that of Glasgow 9·1 per million. The increased amount in the towns is doubtless due to the influence of animal life and to the constant presence in greater proportion than in the country of readily decomposable nitrogenous organic matter in the air (*cf.* Heinrich, Chem. Soc. Abst. 1898, ii. 114).

The quantities of nitrous and nitric acids in the air are even smaller than that of ammonia. Angus Smith (Air and Rain, 287) has given the following results showing the amount contained in a million pts. of rain water :—

Scotland, inland country places .	0·305
Ireland „ „ „ .	0·370
Scotland, country places . .	0·424
„ towns . . .	1·164
England, inland country places .	0·749
„ towns . . .	0·863

Trieschmann found that the average per million brought down in rain at Mount Vernon, Iowa, over a period of 8¼ months was of free ammonia 0·407; albuminoid ammonia, 0·366; nitrates, 0·255; and nitrates 0·018. Rain was found to be richer in nitrogen contents than snow (Chem. News, 1919, 119, 49).

Occasionally, and more especially in the air of towns, minute quantities of hydrocarbons, sulphuretted hydrogen, carbonic oxide, sulphurous acid, common salt, alkaline sulphates, are met with. Boracic acid and sal ammoniac have been observed in air in the neighbourhood of active volcanos.

The percentage amount by volume of the inert gases in the air may be stated as follows :—

Argon	0·93000 p.c.
Krypton . . .	0·00995 „
Xenon	0·00114 „
Neon	0·00123 „
Helium . . .	0·00040 „

(Moissan, Compt. rend. 137, 600; Ramsay, Roy Soc. Proc. 1908, 80 A, 599.)

Organic matter in greater or less quantity is always present in the air. Much of this is nitrogenous, and apparently readily susceptible to putrefaction, giving rise to products which are alternately transformed into ammonia, nitrous and nitric acids. This form of organic matter reduces silver nitrate and potassium permanganate solutions. A portion of the organic matter consists of micro-organisms which are rapidly deposited in the absence of strong aërial currents. Hesse quantitatively estimates the relative proportions of micro-organisms contained in air by aspirating a given volume of the air through glass tubes coated internally with gelatine peptone, which is then kept at a temperature of about 25° for some days, when the various monad bacilli and micrococci which are arrested and which are capable of growing in the gelatine peptone are recognised by the colonies which they form. By means of this method Percy F. Frankland has made a number of estimations of the micro-organisms contained in the air of towns and in the country and in inhabited buildings. By simultaneously exposing small circular glass dishes partially filled with the nutrient gelatine to the action of the air, a rough estimate was obtained not only of the number of micro-organisms in a given volume of the air, but also of the number which fell during a given time on a definite horizontal area. As the mean of a series of observations made on the roof of the South Kensington Museum between January and June, 1886, it was found that there were 35 organisms in 10 litres of air, whilst 279 was the average number which fell on 1 sq. ft. in 1 minute. Similar experiments made near Reigate and in the vicinity of Norwich showed an average of 14 organisms in 10 litres of air, while 79 fell per sq. ft. per minute. Experiments made in Kensington Gardens, Hyde Park, and on Primrose Hill, gave an average of 24 organisms in 10 litres, and a deposition of 85 per sq. ft. per minute. At St. Paul's Cathedral, 56 organisms were found at the base, 29 in the Stone Gallery, and 11 in the Golden Gallery, in 10 litres of air. At Norwich Cathedral, 18 at the base, 9 at a height of 180 ft. and 7 at 300 ft. In inhabited buildings great variations were observed; as a rule, the number of micro-organisms was less than was found in the open air when the air of the room was undisturbed, but rose rapidly when the air was set in motion by draughts or by the presence of many people (P. F. Frankland, Roy. Soc. Proc. 40, 509).

Experiments made at the Montsouris Observatory have shown that far fewer organisms are present in the air during winter than during spring and summer. The number also seems to be greatly increased after rain. Whilst in the warm months the number of spores in 1 litre of air was 28, after heavy rain it rose to 95 and 120.

Atmospheric dust is made up of both inorganic and organic matter. Tissandier found that 1 c.m of the air of Paris contained on the average 7·5 mgms. of dust; after a period of dry weather (8 days), 23·0 mgms., and after heavy rain, only 6·0 mgms. It consisted of from 27 to 34 p.c. volatile matter, and from

66 to 75 p.c. mineral matter, viz. sulphates and chlorides of the alkalis and alkaline earths, oxides of iron, earthy carbonates and phosphates, &c. (*cf.* J. Aitken, Trans. Roy. Soc. Edin. 35, 37, 39).

Radioactive Constituents of the Atmosphere.

A charged electroscope slowly loses its charge in air, and it has been shown that this is not due to moisture, but that, on the contrary, the leakage is greater in dry than in wet weather. The conductivity of air is lessened by passage through a metal tube or by the presence of a weak electric field. These facts indicate that the conductivity of air is due to the presence of charged ions (Townsend, Proc. Roy. Soc. 1899, 65, 192; Geitel, Naturw. Rundsch. 21, 221). The rate of leakage of electricity from a charged conductor in dust-free air is the same for positive and negative charges, but varies with the pressure. The loss of charge per second corresponds to the production of about 20 ions of either sign in each cubic centimetre of air (Wilson, Proc. Roy. Soc. 68, 151).

Elster and Geitel have shown (Wied. Ann. [2] 39, 321) that ions are produced during the formation of ozone by contact of air with flames or by the slow oxidation of phosphorus, &c., but the mere presence of ozone does not impart conductivity to air (Jorissen and Ringer, Ber. 1906, 39, 2090). Langevin (Compt. rend. 1905, 140, 232) states that in air, in addition to ordinary ions carrying charges equal to that of a hydrogen ion in solution, there exist other ions having a much smaller mobility, but carrying charges fifty times as great.

Nordmann has described (Compt. rend. 140, 430) an apparatus for continuously recording the state of ionisation of the air. Air is caused to circulate between the plates of a cylindrical condenser, and the charge given up by the ions is removed by dropping water. The condenser is connected with an electroscope, the deviations of which are recorded photographically, and are proportional to the number of ions present in unit volume of air. Another apparatus for the same purpose is that of Langevin and Moulin (Compt. rend. 140, 305).

No satisfactory explanation of the ionisation of air was found until Elster and Geitel showed (Physikal. Zeitsch. 1901, 76, 590) that a negatively charged wire suspended in the open air became coated with radioactive matter, the presence of which could be proved by its action upon a charged electroscope, although the quantity present was altogether too small to respond to any chemical test. Rutherford and Allan confirmed this observation, and measured the rate of decay of the deposit (Phil. Mag. 1902, vi. 4, 704). Later, Allan showed that the radioactive matter could be removed from the wire by rubbing it with a piece of felt or by solution in ammonia, and that the ashes of the felt or the residue from the evaporation of the solution showed radioactivity having a period of decay equal to that of the deposit on the wire (Phil. Mag. 1904, vi. 7, 140).

These phenomena are due to the presence in the atmosphere of the gaseous emanations of radioactive elements, probably those of radium and thorium (Bumstead, Amer. J. Sci. 1904, 18, 1). The amount of active matter is not constant, but increases with increased circulation of the air, and is therefore probably due to the presence of radium in the soil (Simpson, Phil. Trans. 1905, A, 205, 61). Balloon observations made by Flemming (Zeitsch. physikal. Chem. 1908, 9, 801) show that radium emanation is present even at a height of 3000 metres. Thorium emanation exists principally in air taken from the soil or the lower layers of the atmosphere (Gockel and Wulf, Physikal. Zeitsch. 1908, 9, 907). That it is not widely disseminated in the air is probably due to its rapid rate of decay (Blanc, Physikal. Zeitsch. 1908, 9, 294). The experiments of Dadourian (Physikal. Zeitsch. 1908, 9, 333) and of Wilson (Phil. Mag. 1909, 17, 321) indicate that air normally contains about 3700 times as much radium emanation as thorium emanation.

By passing air through a copper spiral cooled in liquid air, the emanations are condensed, and may then be volatilised into an electroscope and the amount estimated by their effect in ionising the contained air. Ashman (Amer. J. Sci. 1908, 26, 119) has thus found in Chicago air an amount of emanation per cubic metre equal to that which would be in equilibrium with about $1 \cdot 0 \times 10^{-10}$ gram of radium. By absorbing the emanations in charcoal and then volatilising them into an electroscope, Eve has obtained results of the same order—$0 \cdot 8 \times 10^{-10}$ gram for the radium equivalent of the emanation in the air of Montreal (Phil. Mag. 1907, 14, 724), and has shown by numerous observations that the value is not affected by temperature, but that a deep cyclone with rain causes an increase, whilst anti-cyclonic conditions cause a decrease in the amount of emanation (Phil. Mag. 1908, 16, 622). These results have been confirmed by Satterly (Phil. Mag. 16, 584).

All investigators are agreed that these emanations are the chief cause of the ionisation of air, but Wilson, by experiments on the effect of pressure on 'natural' ionisation of air enclosed in a metal cylinder, has shown (Phil. Mag. 1909, 17, 216) that it is partly due to some penetrating radiation the source of which is not in the soil (Pacini, Atti R. Acad. Lincei, 1909, 18, 123). Both Pacini and Wulf (Physikal. Zeitsch. 1909, 10, 152) have detected a double diurnal periodicity in the state of ionisation of the air.

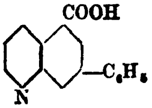
(*See* also Harvey (Physikal. Zeitsch. 1909, 10, 46) and Runge (Chem. Soc. Abstr. 1908, ii. 80).)

ATOMIC WEIGHTS AND SYMBOLS OF THE ELEMENTS (O=16).

Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·9
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	10·9
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·07
Carbon	C	12·005
Cerium	Ce	140·25
Chlorine	Cl	35·46

Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·1
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·7
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	70·1
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·00
Holmium	Ho	163·5
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·84
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·20
Lithium	Li	6·94
Lutecium	Lu	175·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton	Nt	222·4
Nitrogen	N	14·008
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·9
Radium	Ra	226·0
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·06
Tantalum	Ta	181·5
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·15
Thulium	Tm	168·5
Tin	Sn	118·7
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·2
Vanadium	V	51·0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	173·5
Yttrium	Yt	89·33
Zinc	Zn	65·37
Zirconium	Zr	90·6

ATOPHAN. Trade name for 2-phenylquinoline-4-carboxylic acid,



Used as a uric acid eliminant and as an analgesic in the treatment of gout and sciatica.

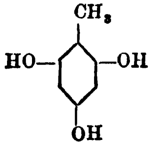
ATOXYL. Trade name for the mono-sodium salt of *p*-aminophenylarsinic acid (Ehrlich and Bertheim). Forms a white crystalline tasteless, odourless powder. So named from its relatively low toxic action (*v.* ARSENICALS, ORGANIC.)

ATRAMENTUM STONE. (*Atramentumstein*, Ger.) A product of the partial oxidation of iron pyrites, consisting of a mixture of ferrous and ferric sulphates with free ferric oxide. Used in the manufacture of ink.

ATRANORIN $C_{19}H_{18}O_8$ is present in the lichens *Evernia vulpina*, *E. prunastri*, *E. furfuracea*, *Lecanora atra*, *L. sordida*, *Parmelia perlata*, *P. physodes*, *P. tinctorium*, *Physcia stellaris*. *Xanthoria parietina*, *Cladonia rangiformis*, *Stereocaulan vesuvianum* and others. It forms colourless prisms, m.p. 195°–197° C. (Zopf), 187°–188° C. (Hesse), easily soluble in hot chloroform, soluble in alkalis with a yellow colour.

According to Paternò, by heating with water to 150°, atranorin gives physciol (methylphloroglucinol) and atraric acid (betorcinolcarboxylic acid methyl ester), and these substances are also obtained when atranorin is heated with acetic acid in a sealed tube (Hesse).

Physciol forms colourless needles, m.p. 104°–105°, gives a blue-green colouration with ferric chloride, and possesses, according to Hesse, the constitution of a methyl-phloroglucinol—

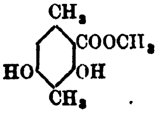


Betorcinol carboxylic acid methyl ester $C_{10}H_{12}O_4$, crystallises in leaflets, m.p. 140°–141° C., and gives a blood-red colouration with calcium hypochlorite solution. Digested with boiling hydriodic acid, it is converted into *β-orcin* (Stenhouse and Groves), $C_8H_{10}O_2$, according to the equation—

$$C_{10}H_{12}O_4+HI=CH_3I+CO_2+C_8H_{10}O_2$$

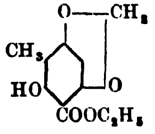
β-orcin (*see* also *barbatic acid*) is 1 : 4-dimethylresorcinol.

The constitution assigned to betorcinol carboxylic acid methyl ester is—



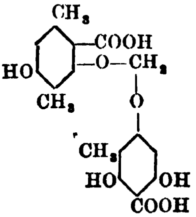
Heated with alcohol in a sealed tube atranorin gives, according to Paternò, *hæmatommic acid* and *hæmatomminic acid*; but the researches of Hesse indicate that these compounds in reality consist of *hæmatommic acid methyl ether* and *betorcinol carboxylic acid methyl ether.*

Hæmatommic acid methyl ether $C_{10}H_{10}O_5$ forms colourless needles, m.p. 147°, soluble in alkaline solutions with a yellow colour. With ferric chloride it gives a purple-red or purple-brown colouration. The *ethyl ether*, $C_{11}H_{12}O_5$, gives colourless needles, melts at 111°–112° (Hesse); 113°–114° (Zopf). It is represented by the formula—



When a solution of atranorin in dilute acetic acid is gently evaporated, *atranorinic acid* (Hesse) is produced. This compound is also present in the *Cladonia rangiformis* (Hesse) when gathered in December, but is absent from the lichen in summer.

Atranorinic acid $C_{18}H_{18}O_9,H_2O$ forms colourless crystals, which are anhydrous at 100°, and then melt at 157°. With ferric chloride it gives a dark brownish-red colouration. With hydriodic acid it gives *β-orcin*, and when heated with alcohol yields carbon dioxide, *physciol* and *β-orcin*. The constitutions assigned to atranorinic acid (1) and atranorin itself (2) are as follows:—



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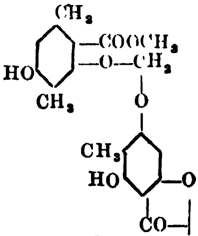


II.

References.—Paternò and Oglialaro (Gazzetta, 7, 289), Paternò (*ibid.*, 10, 157, and 12, 257); Zopf (Annalen, 288, 38); Hesse (J. pr. Chem. 57, 280); Lüdecke (Annalen, 288, 42); Hesse (Annalen, 119, 365); Stenhouse and Groves (Annalen, 203, 302); Hesse (J. pr. Chem. 1906, [ii.] 73, 113). A. G. P.

ATRINAL. Trade name for atropine sulphuric acid.

ATROLACTINIC ACID *v.* LACTIC ACID.

ATROPAMINE. *See* under TROPEINES.

ATROPINE *v.* TROPEINES.

ATROSCINE. *See* HYOSCINE, under TROPEINES.

ATTAR OF ROSES *v.* OILS, ESSENTIAL.

ATYROSYL. syn. for Asyphil.

AUCUBIN *v.* GLUCOSIDES.

AURAMINE. *Iminotetramethyldiparamino-diphenylmethane hydrochloride*, $C_{17}H_{21}N_3,HCl,H_2O$, $NMe_2{\cdot}C_6H_4C(NH){\cdot}C_6H_4{\cdot}NMe_2,HCl,H_2O$ (Graebe), or $Me_2N{\cdot}C_6H_4{\cdot}C(NH_2):C_6H_4:NMe_2Cl,H_2O$ (Stock; Dimroth and Zoeppritz). According to Stock (J. pr. Chem. 47, 401; Ber. 1900, 33, 318), and Dimroth and Zoeppritz (Ber. 1902, 35, 984), the base has the constitution assigned to it by Graebe (Ber. 1899, 32, 1678; 1902, 35, 2615), but the hydrochloride and the other salts have the quinonoid structure $Me_2N{\cdot}C_6H_4{\cdot}C(NH_2){\cdot}C_6H_4:NMe_2Cl$, and are to be regarded as derivatives of triphenylmethane in which an amino- group has replaced one of the benzene residues. (*Cf.* Semper, Annalen, 1911, 381, 234.)

Auramine, the first member of a series of yellow, orange-yellow, or brown dyes, is the hydrochloride of a colourless base obtained by the action of ammonia on tetramethyldiaminobenzophenone, and comes into the market either in the nearly pure form as *Auramine O*, or mixed with dextrin as *Auramine I.* and *II.* (Graebe, Ber. 20, 3264). Fehrmann (Ber. 20, 2847) proposed to restrict the name auramine to the colourless base, but such a change would inevitably lead to confusion; and Graebe (*l.c.*) has consequently adopted the name *auramine-base* for the base itself, using the term auramine in its usual signification.

Preparation.—(1) Auramine was originally prepared from tetramethyldiaminobenzophenone by dissolving it in some indifferent solvent such as chloroform, carbon disulphide, hydrocarbons, &c., treating it with half its weight of phosphorus trichloride or oxychloride, and adding excess of concentrated ammonia to the chlorinated compound thus obtained (B. A. S. F., D. R. P. 27789).

(2) Auramine can be prepared more economically by heating tetramethyldiaminobenzophenone with suitable ammonium salts, such as the chloride, acetate, tartrate, thiocyanate, &c., in the presence of zinc chloride at 200° (B. A. S. F., D. R. P. 29060). Acetamide may be employed instead of ammonium salts (B. A. S. F., D. R. P. 38433), or the dye may be obtained by heating aniline hydrochloride with zinc chloride and carbamide, phenylcarbamide, diphenylcarbamide, or carbanil (Ewer and Pick, D. R. P. 31936); but these alternative methods have no practical importance.

(3) At the present day, auramine is prepared by a method due to Sandmeyer (Eng. Pat. 12549, 1889; 16666, 1890) and Walker (J. Soc. Chem. Ind. 1901, 34), which consists in heating a mixture of tetramethyldiaminodiphenylmethane, sulphur, ammonium chloride, and sodium chloride in a current of dry ammonia. A modification of this method is described by J. Y. Johnson (B. A. S. F., D. R. P. 71320; Eng. Pat. 6249, March 23, 1893), in which the tetramethyldiaminodiphenylmethane is replaced by dimethyl-tetramethyldiaminodiphenylmethane obtained by condensing acetone and dimethylaniline (Ber. 1878, 12, 813). About 14 kilos. of dimethyl-tetramethyldiaminodiphenylmethane are mixed with 120 kilos. of salt, 6 kilos. of sulphur, and 7 kilos. of ammonium chloride, and a stream of ammonia gas is passed through the mixture for eight hours at 175°. The mass is first washed with cold water to dissolve away the salt and ammonium chloride, it is then dissolved in water at 70°, filtered, and the dye salted out, pressed, and dried. Auramine is also prepared by heating dimethylaminobenzamide and dimethylaniline with zinc chloride at 160°–200° (D. R. P. 77329).

(4) Guyot (Compt. rend. 1907, 144, 1219; J. Soc. Chem. Ind. 1908, 679) has synthesised auramines by means of the oxalic esters.

Tetraalkyldiaminodiphenylglycollic esters (J. Soc. Chem. Ind. 1907, 603) form neutral salts with acids, the indigo-blue aqueous solutions of which react with ammonia even when dilute to furnish tetraalkyldiaminodiphenylamino acetic esters, according to the equation:

$$(R_2N{\cdot}C_6H_4)_2CCl{\cdot}CO_2R'+2NH_3$$
$$=NH_4Cl+(R_2N{\cdot}C_6H_4)_2C(NH_2)CO_2R'.$$

These new compounds are *exo*-carboxylic derivatives of the leucauramines, and possess all the properties of the latter. They dissolve in glacial acetic acid with an intense blue colouration, and condense with aromatic tertiary amines to form triphenylmethane derivatives. Thus ethylhexamethyltriaminotriphenyl acetate is produced by heating an equimolecular mixture of dimethylaniline and ethyltetramethyldiaminodiphenylaminoacetate in glacial acetic acid on the water-bath for some minutes:

$$(Me_2N{\cdot}C_6H_4)_2C(CO_2Et){\cdot}NH_2+C_6H_5{\cdot}NMe_2$$
$$=(Me_2N{\cdot}C_6H_4)_2C(CO_2Et)C_6H_4NMe_2+NH_3.$$

When a dilute alkaline solution of the aminoacetic ester is oxidised with dilute potassium ferricyanide solution in the cold, a quantitative yield of the corresponding auramine is produced.

Properties.—Auramine crystallises from water in yellow scales, which seem to consist of six-sided tables, and from alcohol in golden-yellow scales, melts at 267° (Graebe), carbonises at 265°–280° without previous fusion (Fehrmann), and is sparingly soluble in cold but readily soluble in hot water; the temperature of the aqueous solution, however, must not exceed 60°–70°, otherwise decomposition ensues, with the formation of ammonia and tetramethyldiaminobenzophenone. On treatment with mineral acids, the aqueous solution undergoes a similar decomposition either slowly in the cold or very rapidly on heating. Spectroscopically, auramine behaves like most yellow dyes; a hot concentrated aqueous solution, however, shows two bands, one in the red and one in the green, which become broader on dilution and finally coalesce, forming a bright broad band extending from the middle of the red to the commencement of the green (Graebe). On treatment in the cold with ammonia, auramine (crystallised from alcohol) is converted into the colourless base $C_{17}H_{21}N_3$, which melts at 136°, and is characterised by yielding with acids intensely yellow, and for the most part crystalline salts, which dissolve in water and alcohol without fluorescence. Alkaline reducing agents, such as sodium amalgam, slowly decolourise the alcoholic solution of auramine, forming *leucauramine* $C_{17}H_{23}N_3$, a colourless crystalline reduction compound melting at 135°, which dissolves in acetic acid with an intense blue colour owing to its decomposition into ammonia and tetramethyldiaminobenzhydrol.

Auramine dyes wool and silk direct, producing colours which are pure yellow and fairly fast to light and soap. Cotton, for which the dye is chiefly used, requires to be first mordanted with tannin and tartar emetic, and on this account auramine is useful for producing compound shades with other basic colouring matters, such as safranine, benzaldehyde-green, &c., which are fixed by the same mordant. (For further information *v.* Köchlin, Wagner's Jahr. 1884, 1139.)

Salts. *Auramine hydrochloride* $C_{17}H_{21}N_3$, HCl, is sparingly soluble in water, and has μ_∞ 90·4 at 25°; the *palmitate* $C_{17}H_{21}N_3,C_{16}H_{32}O_2$, has m.p. 57°, the *stearate* has m.p. 68° (Gnehm, Röteli Zeit. Angew. Chem. 1898, 487); the *methyl sulphate* obtained by the action of dimethyl sulphate on auramine, has m.p. 225° (Zohlen, J. pr. Chem. 1902, 66, [20] 387).

Substituted Auramines. In addition to auramine, substituted auramines have also been prepared. **Auramine G**, obtained by treating a hot mixture of *sym*-dimethyldiamino-di-*o*-tolylmethane (from methyl *o*-toluidine and formaldehyde) sulphur, ammonium chloride and salt with dry ammonia gas (Gnehm and Wright, U.S. Pat. 488430), has m.p. 120°, the *picrate* has m.p. 234°, the *sulphate* m.p. 182°, the *oxalate* m.p. 210°. *Leucauramine G* has m.p. 208°.

Metaxylylauramine can be obtained by heating an intimate mixture of 10 kilos. of tetramethyldiaminobenzophenone and 23 kilos. of metaxylidine hydrochloride for about 4 hours at 200° in an enamelled vessel provided with a mechanical stirrer. Fusion takes place slowly, and the mass becomes reddish yellow in colour, assuming finally a greenish metallic lustre towards the close of the reaction, which is complete when a test specimen is almost entirely soluble in water. The cooled mass is extracted with hot water, and the dye precipitated in orange-yellow flocks by addition of sodium nitrate to the filtered solution.

Methylauramine $MeN:C(C_6H_4{\cdot}NMe_2)_2$, m.p. 133° (Zohlen, J. pr. Chem. 1902, 66, 387), the *hydrochloride* $C_{18}H_{24}N_3Cl$, has m.p. 225°, the *platinichloride* $(C_{18}H_{24}N_3Cl)_2PtCl_6$, m.p. 190°–200°, the *hydrobromide* $C_{18}H_{24}N_3Br$, m.p. 260°, the *hydriodide* $C_{18}H_{24}N_3I$, m.p. 259°, forms a series of unstable polyiodides: the *trichromate* $(C_{18}H_{24}N_3)_2Cr_3O_{10}$, m.p. 70°, the *thiocyanate* $C_{18}H_{24}N_3CNS$, m.p. 213°–214°, and the *picrate* $C_{18}H_{23}N_3,C_6H_3O_7N_3$, m.p. 225°.

Ethylauramine $EtN:C(C_6H_4{\cdot}NMe_2)_2$, from auramine ethyl iodide and zinc oxide (D. R. P. 136616), m.p. 130°–131°, dyes mordanted cotton a pure yellow.

Phenylauramine $PhN:C(C_6H_4{\cdot}NMe_2)_2$, prepared by heating tetramethyldiaminodiphenylmethane with aniline and sulphur at 200° (Feer, D. R. P. 53614); or by heating dimethylaminobenzanilide with dimethylaniline and phosphorus oxychloride (D. R. P. 44077); has m.p. 172°; the *hydriodide* $C_{23}H_{25}N_3,HI$, has m.p. 242°; the *methiodide* $C_{23}H_{25}N_3,MeI$, has m.p. 214°.

Paraminophenylauramine $NH_2{\cdot}C_6H_4N:C(C_6H_4{\cdot}NMe_2)_2$ (Finckh and Schwimmer, J. pr. Chem. 1894, 50, 401), has m.p. 221°–222°; the *hydrochloride*, m.p. 224°; the *picrate*, m.p. 185°–186° (corr.); the *diacetyl* derivative has m.p. 194°–195°; the *triacetyl* derivative has m.p. 257°–258°; *monobenzoyl* derivative has m.p. 117°; and the *dibenzoyl* derivative has m.p. 180°–181°; *paraphenylenediauramine* $C_6H_4[N:C(C_6H_4{\cdot}NMe_2)_2]_2$, has m.p. 311°–312°.

Orthaminophenylauramine, m.p. 199°–200°, forms a *picrate*, m.p. 220°–221°, and a *benzoyl* derivative, m.p. 236°–237°; *orthophenylenediauramine* has m.p. 305°.

***p*-Tolylauramine**, obtained by heating tetramethyldiaminodiphenylmethane with *p*-toluidine and sulphur (D. R. P. 53614), or from dimethylaminobenzo-*p*-toluidine, dimethylaniline, and phosphorus oxychloride (D. R 44077), has m.p. 178°. **o-Tolylauramine** similarly prepared to the *p*- compound has m.p. 173°–174°, **α-naphthylauramine** $(Me_2N{\cdot}C_6H_4)_2C:NC_{10}H_7$ (D. R. P. 44077), has m.p 225°. **β-naphthylauramine** $(Me_2N{\cdot}C_6H_4)_2C:NC_{10}H_7$ (D. R. P. 44077), m.p. 179°–180°. **Benzylauramine** $C_6H_5{\cdot}CH_2{\cdot}N:C(C_6H_4{\cdot}NMe_2)_2$ (D. R. P. 136616) from auramine benzylchloride and magnesia, has m.p. 116°. **Benzoylauramine** (Fmekh and Schwimmer, J. pr. Chem. 1894, 50, 401) $NBz:C(C_6H_4{\cdot}NMe_2)_2$, has m.p. 179° (corr.).

Methylphenylauramine hydrochloride, *dephenylauramine*, and *pentamethyleneauramine* have been described by Stock (Ber. 1900, 33, 318; J. pr. Chem. 47, 401–413). The following compounds, closely related to the naphthylauramines, form the subject of a patent (D. R. P. 44077): *tetraethyldiaminodiphenylmethylene-α-naphthylamine* $(Et_2N{\cdot}C_6H_4)_2C:N{\cdot}C_{10}H_7$, m.p. 157°–158°; *dimethyldiethyldiaminodiphenylmethylene-α-naphthylamine* $(Me_2N{\cdot}C_6H_4)(Et_2N{\cdot}C_6H_4)C:N{\cdot}C_{10}H_7$, m.p. 177°–178°; *tetraethyldiaminodiphenylmethylene-β-naphthylamine* $(Et_2N{\cdot}C_6H_4)_2C:N{\cdot}C_{10}H_7$, m.p. 155°; *dimethyldiethyldiaminodiphenylmethylene-β-naphthylamine* $(Me_2N{\cdot}C_6H_4)(Et_2N{\cdot}C_6H_4)C:N{\cdot}C_{10}H_7$, m.p. 163°–164°.

The substituted auramines dye silk and wool, and also cotton after mordanting with tannin. The shades produced on cotton are, however, distinctly reddish or brownish-yellow compared with the pure yellow produced by auramine itself; for example, the auramines from orthotoluidine, metaxylidine and cumidine hydrochlorides dye cotton golden-yellow; those from aniline and paratoluidine dye orange-red, that from metaphenylenediamine dyes orange-brown, and those from α- and β-naphthylamine dye brownish-yellow shades (B. A. S. F., D. R. P. 29060; Fehrmann, Ber. 20, 2852).

AURANTIA (*Kaisergelb*) is the commercial name of the ammonium salt of hexanitrodiphenylamine.

Hexanitrodiphenylamine $NH[C_6H_2(NO_2)_3]_2$ is obtained by treating diphenylamine or methyldiphenylamine with nitric acid, and, after the first vigorous action has subsided, heating to complete the reaction. The product is then extracted with water to remove any resin or picric acid associated with it, and finally crystallised from acetic acid.

It forms bright-yellow prisms, melts at 238° with decomposition, but can be sublimed in yellow needles by careful heating, and is almost insoluble in water, more soluble in alcohol, and easily soluble in ether. It readily yields salts, and the *ammonium* salt (aurantia) crystallises in lustrous brown-red needles, although commercially it is obtained as a brick-red powder which dissolves in water and dyes silk and wool a beautiful orange colour (Gnehm, Ber. 7, 1399; 9, 1245; *cf.* Townsend, Ber. 7, 1249; Mertens, Ber. 11, 845). Aurantia is used chiefly as a dye for leather (W. J. 1877, 1002). Like hexanitrodiphenylamine, it is very explosive, but any danger may be avoided by moistening it with glycerol (W. J. 1876, 996). According to Gnehm (Ber. 9, 1246, 1557) and Bayer & Co. (W. J. 1877, 879), aurantia produces skin eruptions; Martius, however, contends that this effect is due to idiosyncrasy, and quotes the opinions of Salkowski and Ziureck in support of his statement (Ber. 9, 1247), and the question appears to have received a solution in this sense in Germany, since the ministerial order of November 8, 1877, prohibiting its manufacture, was cancelled in June, 1880

AURIN and **ROSOLIC ACID** *v.* TRIPHENYLMETHANE COLOURING MATTERS.

AUROCANTAN. Cantharidylethylenediamine aurocyanide.

AUROCHIN. Quinine *p*-aminobenzoate.

AURUM MUSIVUM or **MOSAICUM** *Mosaic gold*. Made by triturating an amalgam of 2 parts tin and 1 of mercury with 1 part sal ammoniac and 1 of sulphur, and subsequently subliming. Used as a bronzing powder for plaster figures (*v.* BRONZE POWDERS).

AUSTENITE. A solid solution of carbon in iron, of variable composition; is a constant constituent of steels containing 1·1 p.c. of carbon or more when cooled rapidly from a temperature of 1100°-1500°. It may be obtained pure by quenching a steel containing 0·93 p.c. carbon and 1·67 p.c. manganese from 1050° in ice-water (Maurer, Métallurgie, 1909, 6, 33). Steels containing 13 p.c. of manganese or 25 p.c. of nickel contain only austenite, and are soft and non-magnetic.

Under the microscope austenite is recognised by its softness as compared with '*martensite*,' with which it is usually associated; by its structureless appearance and by the brightness of an etched, polished section (Le Chatelier, Revue de Métallurgie, 1904)

AUSTRALENE *v.* TURPENTINE.

AUSTRIAN CINNABAR. *Basic lead chromate* (*v.* CHROMIUM).

AUTAN A mixture of solid (polymerised) formaldehyde and the dioxides of barium or strontium, used in the disinfection of living-rooms. On mixing the powder with water, a rapid disengagement of formaldehyde vapour, mixed with oxygen, occurs

AUTOCLAVE An apparatus constructed on the principle of Papin's digester, for heating liquids at temperatures above their boiling points Autoclaves are usually made of cast iron or steel, occasionally of copper, and in some cases of sheet-iron or steel. Cast iron autoclaves are sometimes strapped with steel rings for [illegible] tin, lead, copper, or zinc. Metallic linings are now soldered readily to the [illegible] autoclave. Th[illegible] with a pressure gauge and safety valve, and tubes for the insertion of thermom[illegible] are usu[illegible] by a scr[illegible] cover, working against a wa[illegible] aluminium or copper, and are [illegible] by steam, direct fire, electrical heaters, the circulation of hot oil, or in a bath of molten lead. They are tested before use at (at least) twice their working pressure by means of a hydraulic test pump Occasionally they are provided with agitators working through stuffing [illegible] to

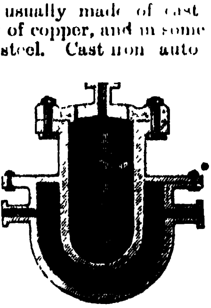


FIG. 1.

ensure thorough mixing of the contents when heated.

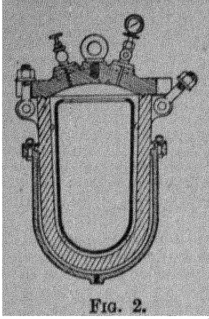


FIG. 2.

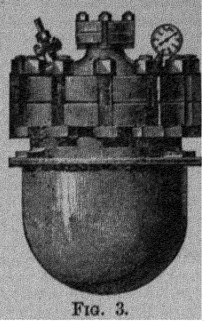


FIG. 3.

Figs 1, 2 and 3 illustrate the types of apparatus for pressures of 20 or 30 atmospheres, but when very high pressures are employed (100 atmos. or more) a tubular design, Fig. 4, is more satisfactory both in cost and ease of manipulation. Autoclaves working at about 10 atmos. are usually of rivetted steel plates, and follow ordinary steam boiler practice. Welding is not as reliable as rivetting, and must always be viewed with suspicion in this class of plant. It is obvious that the ordinary safe working stresses adopted by mechanical engineers are not suitable for designing autoclaves.

Considerations relating to the effect of temperature and chemical action may arise. In the case of cast metal autoclaves the greatest care in design, in selecting the material, and in casting to minimise internal stresses must be taken. When treating liquids, suitable pipes for admission and discharge may make it unnecessary to remove the cover under ordinary circumstances, but when solid substances are charged, the mechanical problem of repeatedly making a tight joint presents itself. Extension of the cover bolts under stress and heat must be considered to avoid leakage under the worst working conditions.

The joint is usually made by means of a tongue in the cover pressing on a soft metal ring in a groove made in the flange of the body. A broad surface is unsuitable and in the case of a copper ring, a bearing area not more than one-eighth inch wide is usually satisfactory at all pressures. Such a joint may be remade hundreds of times without failure. On account of its high elastic limit, nickel steel is the most suitable material for both bodies and bolts of high-pressure autoclaves, and by the use of suitable protective linings can generally be adapted for any chemical process.

When a loose container, as shown in Fig. 2, is employed, the space between the body and the container should be filled with a liquid (paraffin wax is generally most suitable) to improve the rate of heat transference.

J. W. H.

AUTOLYSIS. A physiological term signifying self-destruction, and used to indicate the destructive changes (apart from putrefaction due to micro-organisms) which occur in cells after death or removal from the living body. These changes are due to the action of intra-cellular [illegible] are analagous to those which occur in digestion; indeed the term auto-digestion is sometimes employed. The study of such changes is important be[illegible]lieved that [illegible] after death, w[illegible]ls are still [illegible] a time, a[illegible] with those which occur during life and result in the formation of waste substances, the products of vital activity. During life, however, the destructive changes are counterbalanced by changes in the opposite direction by which the cells build themselves up from food materials to repair their wear and tear. Assimilation of this kind is obviously impossible after death.

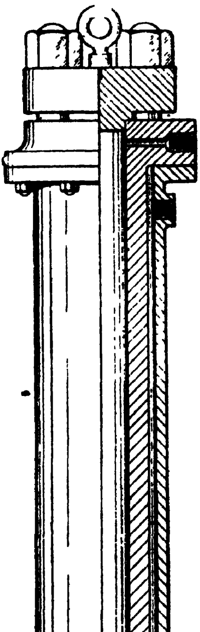


FIG. 4.

AUTUNITE or CALCO-URANITE. A mineral consisting of hydrated phosphate of uranium and calcium $Ca(UO_2)_2P_2O_8 \cdot 8H_2O$, which within recent years has been somewhat extensively mined as an ore of uranium and radium. It is a member of the isomorphous group of minerals known as the 'uranium micas,' which crystallise in square, tetragonal (or very nearly square, orthorhombic) plates with a perfect micaceous and pearly cleavage parallel to their surface. In the orthorhombic autunite the colour is characteristically sulphur-yellow, or sometimes with a greenish tinge, so that this mineral is readily distinguished from the emerald-green torbernite or cupro-uranite. Sp.gr. 3·1; H. 2–2½. It occurs as an alteration product of pitchblende, and is often found as a scaly encrustation on the joint-planes of weathered granite or gneiss. The more important localities are St. Symphorien, near Autun in France (hence the name autunite); St. Just, Redruth, and Grampound Road in Cornwall; Johanngeorgenstadt and Falkenstein in Saxony; Black Hills in South Dakota; Olary and Mount Painter in South Australia; and Sabugal, near Guarda in Portugal. At the last-named locality several mines have recently been opened up; the crude ore is here leached with sulphuric acid, and the extracts sent to Paris for further treatment. L. J. S.

AUXOCHROME *v.* COLOUR and CHEMICAL CONSTITUTION.

AVA or *Kava-kava.* The root of *Piper methysticum* (Forst, f.), growing in the islands of the Pacific. It is taken as an intoxicant by the natives, and is used as a drug on the Continent. It is often adulterated with matico and annatto (Pharm. J. [3] 7, 149).

AVENTURINE or **AVANTURINE.** A variety of quartz found at Capa de Gata, Spain, spangled throughout with minute yellow scales of mica, is known as aventurine quartz. An aventurine felspar or sunstone is found at Tvedestrand, Norway. It is used for ornaments.

Artificial aventurine, or *glass,* or *gold flux,* was manufactured for a long period at the glass-works of Murano, near Venice. It may be prepared by adding to 100 parts of a not too refractory glass, 8 to 10 parts of a mixture of equal parts of ferrous and cuprous oxides, and allowing the mixture to cool very slowly so as to facilitate the formation of crystals.

Aventurine glaze for porcelain, invented by Wöhler (Annalen, 70, 57), is prepared by finely grinding 31 parts Halle kaolin, 43 quartz sand, 14 gypsum, and 12 porcelain fragments; making the whole into a paste with 300 parts water, and adding successively 19 parts potassium dichromate, 47 lead acetate, 100 ferrous sulphate, and sufficient ammonia to precipitate the whole of the iron. After the soluble potash and ammonium salts have been washed out, the glazing is ready for use.

AVIGNON GRAINS. The seeds of *Rhamnus infectorius,* employed in dyeing for the production of yellow colours (*v. Rhamnin,* art. XANTHORHAMNIN).

AVOCADO PEAR or **ALLIGATOR PEAR.** The fruit of *Persea gratissima,* a tropical product. The fruit, which usually weighs from 4 to 6 oz., consists of rind (about 8 p.c.), flesh (67 p c.), and a large 'stone' or 'pit' (about 25 p.c.). According to Prinsen-Geerlings (Chem. Zeit. 1897, 21, 715), the flesh contains:

Glucose	Fructose	Saccharose	Total sugar
0·40	0·46	0·86	1·72

The flesh, which has a nut-like flavour, is usually eaten with pepper and salt. An analysis, made by Jamieson (Chem. News, 1910, 102, 61), gave:

Water	Ether extract	Protein	Sugar	Fibre	Ash
66·9	10·6	5·7	1·1	4·0	2·0

The ether extract was green, and contained about 4 p.c. of resins. After their removal, an oil, resembling that of bergamot, was obtained, which had an iodine value of 29·9, and saponification value of 207. La Forge (J. Biol. Chem. 1916, 24) found that the sugar present in the pulp of the ripe fruit could be extracted with water and crystallises from dilute alcohol in hexagonal prisms, m.p. 152°. It is non-fermentable and not oxidised by bromine, and is probably mannoketoheptose. H. I.

AVOCADO PEAR, OIL OF. An oil obtained from the oleaginous fruit of the *Persea gratissima.* Hofmann stated that for the purposes of the soapmaker this oil would be as valuable as palm oil.

AWAL or *Tarwar.* An Indian drug, the bark of *Cassia auriculata* (Linn.) (Dymock, Pharm. J. [3] 7, 977).

AWLA *v.* AMLAKI.

AXIN. A waxy secretion of a Mexican rhynchotrous insect *Llaveia axinus* which feeds on *Spondias lutea, Xanthoxylum Clava-herculis,* and *X. pentanome:* has the consistence of butter, the smell of rancid fat, and a yellow colour. Melts at 35°, and is soluble in hot alcohol and ether. Rapidly absorbs oxygen from the air, becoming brown, hard and insoluble in alcohol and ether. Is readily saponified, yielding *axinic acid* and glycerol. It resembles Japan lac and forms an excellent lacquer for wood, metals, and pottery (Bocquillon, J. Pharm. Chim. 1910, 2, 406; J. Soc. Chem. Ind. 29, 1320).

AXINITE. A complex borosilicate of aluminium, calcium, iron and manganese. Various formulæ have been proposed: W. E. Ford (1903) gives $R''_7R'''_4B_2(SiO_4)_8$, where R''=Ca, Fe, Mn, Mg, H_2, and R'''=Al, Fe. According to W. T. Schaller (1909) the composition is expressed as isomorphous mixtures of 'ferro-axinite' $4CaO{\cdot}2FeO{\cdot}2Al_2O_3{\cdot}B_2O_3{\cdot}8SiO_2{\cdot}H_2O$, and 'manganaxinite' $4CaO{\cdot}2MnO{\cdot}2Al_2O_3{\cdot}B_2O_3{\cdot}8SiO_2{\cdot}H_2O$. The mineral contains 5–6 p.c. B_2O_3. Crystals are triclinic with a characteristic axe-shaped habit, hence the name. The colour is usually clove brown, but may be yellowish or greenish. D 3·03–3·36, H 6½–7. Axinite occurs in crystalline schists and metamorphic rocks at many localities. Fine crystals, suitable for cutting as gem-stones, are not uncommon from Bourg d'Oisans, Isère, France, and large groups of crystals come from Japan. In the metamorphic rocks surrounding the granite mass of Bodmin, in Cornwall, massive axinite and axinite-rock are of abundant occurrence (G. Barrow, Mineralog. Mag. 1908, xv. 113; Geology of Bodmin and St. Austell, Mem. Geol. Survey, 1909).

Tourmaline (*q.v.*), another complex borosilicate containing rather more boron (B_2O_3 9–11 p.c.), is also of common occurrence under the same conditions in Cornwall. It is possible that these occurrences may be of use as a source of boron. L. J. S.

AZADIRACHTA, *Margosa,* or *Nim.* The bark of the nim tree, *Melia indica* (Brandis) [*M. Azadirachta*], is commonly used in India as a tonic and febrifuge. It contains a bitter resin. An oil, used in medicine and for burning is expressed from the seeds, which on saponification yielded 35 p.c. of fatty acid melting at 30°, and 65 p.c. melting at 44°.

AZAFRAN or **AZAFRANILLO.** The root of a plant obtained from Paraguay, belonging to the family of the *Scrophulariaceæ,* used to colour fats. Contains about 1 p.c. of a dye (*azafrin*) easily extracted by boiling benzene. Forms orange-red crusts of microscopic needles, m.p. 214°. Does not contain nitrogen or methoxy- or ethoxy- groups; one hydroxyl group is shown by Zerewitinoff's method. Dyes wool yellow, and forms yellow to orange lakes with Scheurer's mordants; wool extracts the whole of the dye from a hyposulphite vat. Gives a fine blue solution in concentrated sulphuric acid, which becomes violet on adding alcohol (Liebermann, Ber. 1911, 44, 850). It is not identical with bixin, as conjectured by van Hasselt, in spite of the similarity in their reactions. The acid reactions of azafrin afford a good example of halochromism. Methyl-azafrin, obtained by the action of dimethyl-sulphate, gives a series of salts parallel with those of the parent substance (Liebermann and Schiller, Ber. 1913, 46, 1973).

AZELAIC ACID. *Lepargylic acid.* $CO_2H\cdot(CH_2)_7\cdot CO_2H$. It is obtained by oxidising Chinese wax (Buckton, J. 1857, 303), cocoanut oil (Wirz, Annalen, 104, 261), or castor oil (Arppe, Annalen, 124, 86) with nitric acid; by the oxidation of oleic acid with potassium permanganate and caustic potash (Ehmed, Chem. Soc. Trans. 1898, 627), and by the oxidation of keratin (horn shavings) with permanganate (Lissizin, Zeitsch. physiol. Chem. 1909, 226). It is formed together with other products when fats or oleic acid become rancid (Scala, Chem. Zentr. 1898, i. 439). It has been synthesised from pentamethylene bromide and sodium acetoacetate (Haworth and Perkin, Chem. Soc. Trans. 1894, 86), and has been obtained by decomposing the ozonide of oleic acid (Molinari and Soncini, Ber. 1906, 2735; Harries and Thieme, *ibid.* 1906, 2844; Molinari and Fenaroli, *ibid.* 1908, 2789). It is best prepared by oxidising with potassium permanganate an alkaline solution of ricinoleic acid obtained by the hydrolysis of castor oil (Maquenne, Bull. Soc. chim. 1899, (iii.) 21, 106; Hazura and Grüssner, Monatsh. 9, 475). Azelaic acid crystallises in colourless plates, m.p. 106·2° (Massol, Bull. Soc. chim. [3] 19, 301), and is readily soluble in alcohol, less soluble in water or ether. By heating azelaic acid with soda lime, *azelaone* (*cyclononanone*) $C_8H_{14}O$, b.p. 205° (*circa*), is obtained (Miller and Tschitschkin, Chem. Zentr. 1899, ii. 181); Harris and Tank (Ber. 1907, 4555) have shown that a complex mixture of cycloketones is obtained by distilling the calcium salt of azelaic acid. *Azelaic anhydride* is obtained by heating azelaic acid with 7–8 pts. of acetyl chloride. It melts at 56°–57° (Étaix, Ann. Chim. Phys. [7] 9, 399).

AZELAONE *v.* AZELAIC ACID.

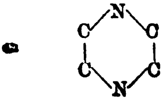
AZIDINE BLACK, -BLUE, -BORDEAUX, -BROWN, -FAST RED, -FAST SCARLET, -GREEN, -ORANGE, -PURPURINE, -YELLOW, -VIOLET, -WOOL BLUE *v.* AZO- COLOURING MATTERS.

AZIMINOBENZENE *v.* DIAZO COMPOUNDS.

AZIMINONAPHTHALENES *v.* DIAZO COMPOUNDS.

AZINES (Quinoxalines). Azonium bases, and colouring matters derived from them.

Definition.—The term 'azines' has been given to a group of organic bases, which contain in their molecule as an intrinsic part of their constitution a heterocyclic hexagonal ring, built up of four carbon and two nitrogen atoms, arranged in such a manner that the nitrogen atoms stand in para-position to each other, whilst the four carbon atoms are disposed in two pairs between them, thus:



The term 'azine,' first proposed by Merz, is not happily chosen, and is even misleading, as it enters into the names of other nitrogen compounds of a different constitution, such as the hydrazines.

The name 'quinoxaline' was given by Hinsberg to compounds which also correspond with the above definition. It was, therefore, considered for some time as synonymous with the word 'azine,' which latter was, however, more frequently used. In later years it has become customary to distinguish between the two terms, and to use them for the two tautomeric forms in which these bases occur (*see Theory*).

The name 'azonium bases' has been given by Witt to a class of organic bases, derived from the azines by the linking of an organic radicle to one of the nitrogen atoms, whereby this atom passes from the trivalent into the pentavalent state, a process which results in a very marked change of the properties of the substance.

Both the azines and azonium bases possess the nature of powerful chromogens, the heterocyclic ring above mentioned being endowed with strong chromophoric properties. Being highly basic and capable of assuming a quinonoid structure (*see Theory*), they, and especially the azonium bases, possess to some extent the nature of dyestuffs, which is, however, much more strongly developed by the introduction of separate auxochromic groups. A very large number of powerful colouring matters of great intensity, variation, and purity of shade may thus be obtained, some of which have acquired considerable practical importance. According to their constitution, which is in almost all cases completely cleared up, they have been classified into groups, which have received the names **eurhodines**, **eurhodols**, **safranines**, **safranols**, **aposafranines**, **indulines**, and **fluorindines**.

The investigation of the azines and their derivatives, which was accomplished by a number of chemists during the last 20 years of the nineteenth century, has been of considerable importance in the development of our present views on the constitution of colouring matters, and especially in the adoption of the modern quinonoid structural formulæ for the great majority of them.

History.—The two simplest and most typical members of the azine group, diphenazine and dinaphtazine, have been known for many years as 'azophenylene' (Claus and Rasenack, 1873; Annalen, 168, 1) and 'naphtase' (Laurent, 1835; Ann. Chim. Phys. 59, 384), but their constitution was not properly understood and their importance not recognised. Merz (1886, Ber. 19, 725) finally proved the constitution of the former, which had been insufficiently substantiated by Claus, and proposed for it the name diphenazine; Witt (1886, Ber. 19, 2791) determined the true nature of 'naphtase.' In 1884 Hinsberg (Ber. 17, 319) described a general method for preparing his quinoxalines, which proved most fruitful in the further development of the subject. Other general methods were discovered by Witt, Merz, Japp, Ullmann, and others.

The first eurhodines were prepared by Witt in 1879 and 1885. He recognised that they formed a new class of dyestuffs, and also that they were related to the safranines. He determined their constitution in 1886 (Ber. 19, 441) by showing that they are the amino- derivatives of the azines or quinoxalines. At the same time he discovered the first eurhodol. The natural consequence of this discovery was the clearing up of the nature of the safranines, which were recognised in the same year simultaneously and independently by Witt, Nietzki, and Bernthsen as diamino- derivatives of the (then hypothetical) azonium bases. The first representative of this new class of bases was prepared in 1887 by Witt (Ber. 20, 1183).

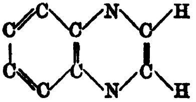
The subject was now taken up and rapidly advanced by many chemists, amongst whom Nietzki and his collaborators, Kehrmann, Ullmann, and their collaborators, may be cited. Otto Fischer and Hepp also did a considerable amount of work in this domain, and especially in the investigation of the indulines and aposafranines.

The typical indulines and safranines have been discovered by purely empirical methods in the early days of the colour industry. The simplest representative of the group, *phenosafranine*, was prepared by Witt in 1877. Its phenylated derivative is *mauveïne*, the first artificial dyestuff prepared by W. H. Perkin in 1856.

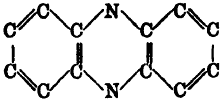
Theory.—It has been already stated that the essential part of the molecule of an azine is the heterocyclic ring consisting of two atoms of nitrogen and four of carbon. Each of these six atoms has three valencies engaged in the formation of the ring; the nitrogen atoms have, therefore, no free valencies left (so long as they remain in the trivalent condition), whilst each of the carbon atoms has one valency free to be saturated by hydrogen or another monovalent element or radicle. The simplest possible compound of the kind would thus have the formula $C_4N_2H_4$. It seems natural to suppose that it would be the prototype of all the azines.

Such a compound exists and is well known. It has received the name *pyrazine*. Many derivatives of it, formed by the substitution of its hydrogen atoms by monovalent organic radicles are also known; they form the large and well-investigated class of the ketine or aldine bases. But neither pyrazine itself (which in its properties resembles pyridine, to which it stands in the same relation as pyridine stands to benzene) nor the ketines show any resemblance to the typical azines. They exhibit no colourations, nor do they form any derivatives which have the nature of dyestuffs. For this reason pyrazine and the ketines are no longer considered as belonging to the azine group.

The characteristic properties of the azines only appear in compounds in which at least one other ring system is linked to the pyrazine ring, in such manner that one of the C_2-groups of the latter becomes part of an aromatic radicle. The process may be repeated. Thus the simplest representatives of the azine group would be compounds of the following type :—



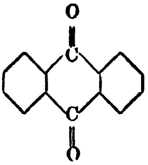
Phenazine.



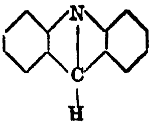
Diphenazine.

The nomenclature of the true azines has been chosen accordingly. The aromatic radicle or radicles linked to the central (or 'meso-') ring are prefixed to the syllables -azine.

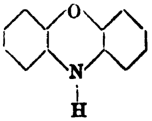
The azines are members of the aromatic series. If we consider them as such, we recognise at once a strong analogy to other substances which contain heterocyclic rings linked to aromatic radicles, such as:



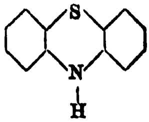
Anthraquinone.



Acridine.



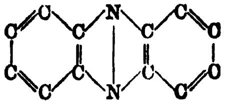
Oxazine.



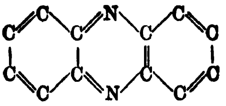
Thiazine.

all of which are chromogens, like the azines.

If we consider the manner in which the six atomicities of the two nitrogen atoms contained in the meso- ring of an azine may be disposed, we recognise two possibilities which are represented in the following structural formulæ of diphenazine :—



I.



II.

Formula I. is the one first proposed by Claus for his 'azophenylene,' and by Merz for his azines; II., the one suggested by Hinsberg for his quinoxalines. Practically, there is no difference between azines and quinoxalines; they form one group; but it has been for a long time a matter of opinion which of the above formulæ was more adapted to the properties of these substances. Formula I. explains by its perfect symmetry the extreme stability of the azines, the fact that they may all be distilled without the slightest decomposition at extremely high temperatures. Formula II., on the other hand, is distinctly (ortho-) quinonoid, and consequently suggestive of chromogenic properties.

The existing difference of opinion as to the constitution of the azines has been finally disposed of by the admission that the azines are undoubtedly tautomeric, capable of assuming either of the constitutions I. and II., according to circumstances. In their free state, in which they are volatile and almost colourless, they possess the symmetrical (azine) constitution I., whereas in their intensely coloured salts they have more probably the asymmetrical, quinonoid (quinoxaline-) constitution II. In the colouring matters derived from the azines, the case is frequently complicated by the fact that the auxochromic groups participate in the formation of the quinonoid constitution, which, by that means, may become *para*- as well as *ortho*-quinoid. Sometimes it is difficult to decide between the existing possibilities.

Synthetical methods for the production of azines, and their derivatives and description of some typical representatives of the group.

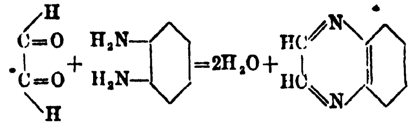
I. **Azines.** (*a*) *Synthetical methods.* (These will be referred to in the description of typical representatives by their number.)

1. By heating α-nitronaphthalene with powdered quicklime, Laurent (Ann. Chim. Phys. 59, 384) obtained dinaphthazine, which he called naphthase. Doer (Ber. 3, 291) and Klobukowski (Ber. 10, 573) modified the method by replacing the quicklime by zinc-dust. Schichuzky (J. R. 6, 2464) used lead oxide.

Wohl and Aue (Ber. 34, 2443) observed (1901) that nitrobenzene gives considerable quantities of diphenazine on being heated with strong caustic soda, a reaction which is practically identical with the one discovered by Laurent.

2. Claus and Rasenack (Annalen, 168, 1) obtained 'azophenylene' (diphenazine) by the dry distillation of orthoazobenzoic acid in the shape of its calcium or potassium salt. Claus proposed the azine formula for his product, but failed to afford convincing proofs for it.

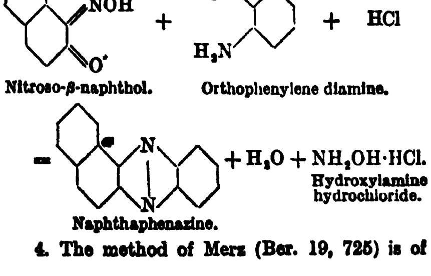
3. A general method of great applicability was indicated by Hinsberg (Ber. 17, 319; 18, 1228), who showed that whenever an *alpha*- or *ortho*-diketone reacts on an aromatic orthodiamine, two molecules of water are given off and an azine is formed. The method was first applied to the production of phenazine:



Glyoxal. *o*-Phenylenediamine. Phenazine (quinoxaline).

It works in most cases so well, that it has been recommended by its author (Annalen, 273, 343, 371) as the best method of identifying either an orthodiamine or an orthodiketone. Very small quantities of the ingredients are necessary, and the azine formed is easily recognised by its melting-point and sulphuric acid reaction.

Hinsberg's reaction may be extended to nitroso-β-naphthol, which is in reality the oxime of ortho-naphthaquinone. Ullmann and Heisler obtained (Ber. 42, 4263) naphthaphenazine by heating ortho-phenylenediamine hydrochloride with nitroso-β-naphthol:

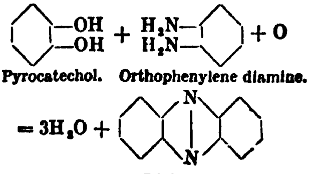


Nitroso-β-naphthol. Orthophenylene diamine.

Hydroxylamine hydrochloride.

Naphthaphenazine.

4. The method of Merz (Ber. 19, 725) is of less general application. It consists in the action of orthodihydroxyl- derivatives upon orthodiamines: the hydro- derivatives of the azines are formed, and these are oxidised by the oxygen of the air into the azines:

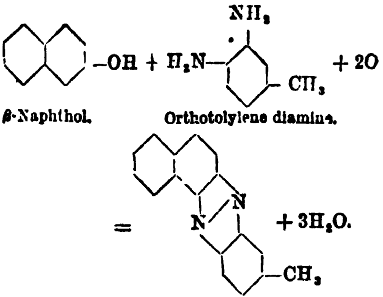


Pyrocatechol. Orthophenylene diamine.

Diphenazine.

5. Early investigators had studied the reaction of ammonia under pressure upon benzoin (Erdmann, Annalen, 135, 181) and phenanthraquinone (Sommaruga, Monatsh. 1, 146). Japp and Burton showed that the free ammonia may be advantageously replaced by ammonium acetate, and proved that the 'ditolane azotide' and 'phenanthrene azotide' obtained were tetraphenylketine and diphenanthrazine. They generalised the method and applied it to β-naphthaquinone, from which they obtained dinaphthazine (Chem. Soc. Trans. 1887, 98).

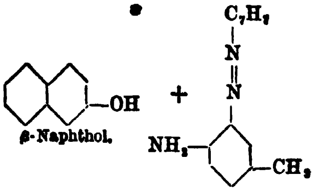
6. Another mode of formation of the azines consists in the joint oxidation of a phenol, in which the *para*- position is no longer open to substitution, and aromatic orthodiamines. This method was discovered by Witt (Ber. 19, 917), who used it for the production of a new isomeride of tolunaphthazine by oxidising a mixture of β-naphthol and orthotolylene diamine:



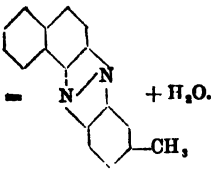
β-Naphthol. Orthotolylene diamine.

Tolunaphthazine.

7. An elegant modification of the above method was devised in 1905 by Ullmann and Ankersmit (Ber. 38, 1811), who heated β-naphthol with orthoaminoazotoluene. The latter takes up the hydrogen liberated in the reaction, yielding at the same time the necessary orthodiamine.

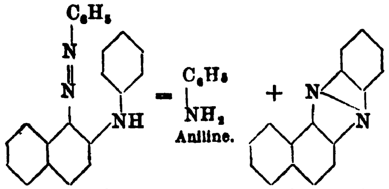


β-Naphthol. Orthoaminoazotoluene.



Tolunaphthazine.

8 A very peculiar mode of formation of these substances was discovered by Witt (Ber. 20, 571), who showed that the orthoazo- derivatives of secondary amines, and more especially of such amines containing the β-naphthyl- group, are decomposed by being heated with acids into the corresponding azine and amino- compound, thus:



Benzene-azo-phenyl-β-naphthylamine. Aniline. Naphthaphenazine.

The reaction is simple and easy, and gives, as a rule, excellent yields. It is in reality a condensation of the secondary amine into the corresponding azine by the dehydrogenating influence of the azo- group temporarily introduced for the purpose.

(*b*) *Generic characters of the azine group.* All azines have certain peculiar properties in common. As a rule, they are solid, well crystallised compounds of white, pale yellow, or even orange colour, possessing a high melting-point, and boiling under atmospheric pressure at very high temperatures (in some cases approaching red heat) practically without decomposition. They sublime at temperatures below their boiling-point, and their vapours condense into voluminous aggregates of crystals.

All the azines are bases which form salts with acids. The mono-acid salts, with the stronger mineral acids, may generally be obtained in a crystallised condition; but they are stable only in the presence of an excess of acid or in the absence of water, which easily decomposes them into their constituents. These salts are intensely coloured, a fact which justifies the inference that they contain the base in the quinonoid (quinoxaline) form. The hydrolytic action of the water is therefore accompanied by the tautomeric change into the symmetrical (azine) form. These salts, some of which have been analysed, invariably contain one equivalent of acid for one molecule of the base. The di-acid salts cannot be isolated, but evidence of their existence is given by the intense red, violet, or blue colourations exhibited by the solutions of azines in a great excess of strong acid, preferably sulphuric acid. If water be added to these solutions, a change takes place; the di-acid salt is decomposed, the yellow or orange mono-acid salt is formed, and, on further addition of a large excess of water, the free azine itself separates out in flakes. These striking colour reactions are highly characteristic, and form the best means of identifying the azines.

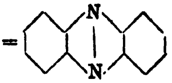
Notwithstanding these intense colourations, the azines are not applicable as dyestuffs. They are only to be considered as chromogens and suitable to produce colouring matters by the introduction of auxochromic groups into their molecules. They are thus strictly analogous to the other heterocyclic chromogens such as anthraquinone, acridine, oxazine, and thiazine.

There is, however, one group of azines to which all the rules and general characteristics given above cannot very well be applied. These are the 'Indanthrenes,' certain azines of the anthracene group, which, owing to their large molecule and very complicated constitution, possess properties quite different from all the other azines. They are intensely coloured and extremely valuable as dyestuffs if applied to the textile fibre by the 'vat process' like indigo. This peculiar mode of application brings them into close relationship with indigo, and they will therefore be treated in this work under INDIGO AND INDIGOID DYESTUFFS (*q.v.*).

(*c*) *Description of some typical representatives of the azine group.*

Diphenazine

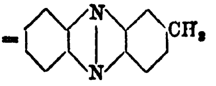
$C_{12}H_8N_2$ =



(Claus, Annalen, 168, 1; Bernthsen, Ber. 10, 3256; Ris, Ber. 19, 2206; Wohl, Ber. 34, 2443) has been obtained by the methods 1, 2, and 4. It forms pale-yellow needles, of the m.p. 170°-171°, soluble in alcohol and most other solvents. It distils without decomposition. It dissolves in strong acids, forming unstable salts of yellow and red colour.

Toluphenazine

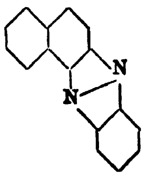
$C_{13}H_{10}N_2$ =



has been prepared by Merz (Ber. 19, 725) by th action of pyrocatechol on orthotolylenediamin (method 4). It is very similar to diphenazin Its m.p. is 117°, its b.p. 350°.

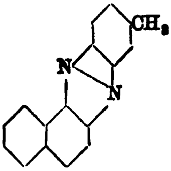
Naphthaphenazine

$C_{16}H_{10}N_2$ =

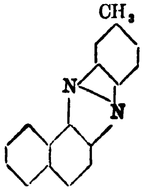


has been prepared by Witt (Ber. 20, 571). Th best mode of obtaining it is by the decomposi tion, by acid, of the azo- compounds derived fror phenyl-β-naphthylamine, but it has also bee prepared by the action of β-naphthaquinone o orthophenylenediamine and by simultaneou oxidation of the latter and β-naphthol. It form yellow needles, melting at 142·5°, distilling at high temperature without decomposition, an dissolving in sulphuric acid with a reddish-brow colouration. On dilution, two sulphates crystal lise from this solution. It is supposed that th formation of two series of monacid salts of thi base is due to either of the two nitrogen atoms becoming pentavalent and saturated with the acid.

Tolunaphthazines $C_{17}H_{12}N_2$. Three substances of this formula are known, the isomerism of which has been discussed by Witt (Ber. 20, 577). One of these, melting at 179·8° has been prepared by the simultaneous oxidation (Ber. 19, 917) of orthotolylenediamine and β-naphthol (methods 6 and 7). Its constitution is expressed by the formula



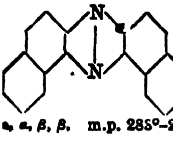
It dissolves in sulphuric acid with a violet colouration. The other is formed by the decomposition by acids of the azo- derivatives of paratolyl-β-naphthylamine (Ber. 20, 577) (method 8). Its constitution is represented by the formula



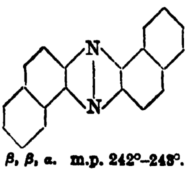
Its melting-point is 169°; its sulphuric acid reaction is similar to that of naphthaphenazine. The third tolunaphthazine, discovered by Hinsberg (Annalen, 237, 343*a*, 371) (method 3), has been proved to consist of a molecular combination of the two preceding ones; its melting-point is 139°–142°.

Several other tolunaphthazines are theoretically possible. They have not, however, hitherto been prepared.

Dinaphthazines $C_{20}H_{12}N_2$. It has already been stated that Laurent's mysterious 'naphthase,' prepared by method 1, finally proved to be dinaphthazine. It is probable that Laurent's product was a molecular combination of two of the four isomeric dinaphthazines foreseen by theory. A similar mixture may be obtained by reacting with αβ-naphthylenediamine upon β-naphthaquinone (method 2). This method was used by Witt in his identification of Laurent's 'naphthase' (Ber. 19, 2791). For preparing the constituents of this mixture in a pure state the synthetical method 8 should be resorted to; it consists in the decomposition of the azo- derivatives of the two isomeric (α, β, and ββ)-dinaphthylamines (Matthes, Ber. 23, 1329 and 1333). The compounds thus obtained have the following constitutions and melting-points:—

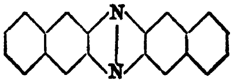


α, α, β, β. m.p. 283°–284°.

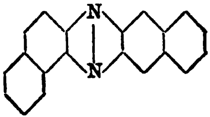


α, β, β, α. m.p. 242°–243°.

The two other possible isomerides:



β, β, β, β.

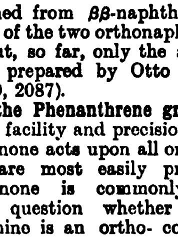


α, β, β, β. m.p. 240°

may be obtained from ββ-naphthylenediamine by the reaction of the two orthonaphthaquinones (method 2), but, so far, only the asymmetrical one has been prepared by Otto Fischer and Albert (Ber. 29, 2087).

Azines of the Phenanthrene group. Owing to the extreme facility and precision with which phenanthraquinone acts upon all orthodiamines, these azines are most easily prepared, and phenanthraquinone is commonly used for deciding the question whether any given aromatic diamine is an ortho- compound. A large number of azines has thus become known, of which only a few may be described as typical representatives of the group.

Phenanthraphenazine $C_{20}H_{12}N_2$ (isomeric with dinaphthazine) may be obtained by acting on orthophenylenediamine with either phenanthraquinone in an acetic acid solution (Hinsberg, Annalen, 237, 340), or with phenanthraquinone sodium bisulphite in an aqueous solution (method 2). It crystallises in pale-yellow needles, melting at 217°, and dissolves in sulphuric acid with a beautiful red colouration. Its constitution is



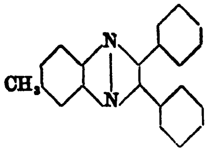
A similar substance may be obtained from orthotolylenediamine. It melts at 212°–213°.

Phenanthranaphthazine $C_{24}H_{14}N_2$ is easily obtained (Lawson, Ber. 18, 2426) from orthonaphthylenediamine and phenanthraquinone (method 2). It gives a violet colouration with sulphuric acid. M.p. 273°. The sulphonic acid derivatives of this substance, $C_{24}H_{13}N_2 \cdot SO_3H$, are obtained (Witt, Ber. 19, 1719; 21, 3485 *seq.*) by acting with an aqueous solution of phenanthraquinone sodium bisulphite upon the solutions of the various naphthylenediamine sulphonic acids in sodium acetate solution, acidulated with acetic acid. These sodium salts are soluble in pure water; very small quantities of alkaline salts are sufficient to precipitate them from these solutions.

Chrysotoluazine $C_{25}H_{16}N_2$ and **Chrysonaphthazine** $C_{28}H_{16}N_2$ have been prepared by Liebermann and Witt (Ber. 20, 2442) from chrysoquinone and the corresponding orthodiamines (method 2). The same authors obtained azine derivatives from the quinone of picene.

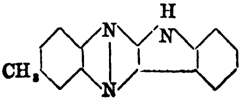
Tolustilbazine $C_{21}H_{18}N_2$ was discovered by Hinsberg, who described it under the somewhat misleading name 'Diphenyltoluquinoxaline' (Annalen, 237, 339). It is typical of the many azines which may be obtained by the action of benzil upon aromatic orthodiamines.

It separates in silvery leaflets from an alcoholic solution of benzil mixed with a solution of orthotolylenediamine (method 2). It melts at 111°, and dissolves with a crimson shade in sulphuric acid. Its constitution is expressed by the formula



The corresponding derivative of orthonaphthylenediamine was prepared by Lawson (Ber. 18, 2426).

Toluindazine $C_{15}H_{11}N_3$, the azine derivative of isatine, has been prepared by Hinsberg (Annalen, 237, 344) from orthotolylenediamine and isatin, by melting together the ingredients (method 2) and crystallising the product obtained from a mixture of alcohol and acetic acid. It forms yellow needles, melting at 290°, and dissolving in acids with a brownish-red colouration. Its constitution is expressed by the formula



A large number of other less important azines have been prepared in experiments made with a view to showing that certain compounds obtained by the authors were either orthodiketones or orthodiamines.

II. Colouring matters derived from azines (eurhodines and eurhodols).

It has already been said that by the introduction of an auxochromic group, NH_2 or OH, into the molecule of an azine, the latter is transformed into a colouring matter. The amino-derivatives of azines containing either one or several amino- groups, are embraced by the generic name of *eurhodines*, whilst the name of *eurhodols* has been given to the phenolic (OH) derivatives of the azines. The following is an enumeration of the various methods by which eurhodines and eurhodols have been obtained:—

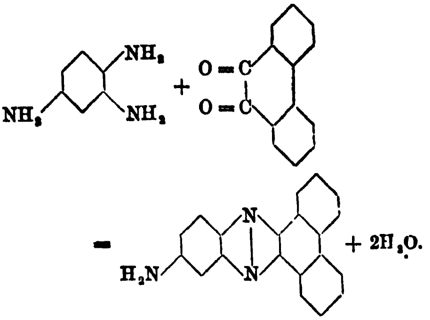
A. EURHODINES.

1. By heating together any orthamino-azo-compound and the hydrochloride of certain aromatic monoamines, such as, for instance, α-naphthylamine or α-aminoquinoline, preferably in a phenol solution, monoamino-azines (the eurhodines proper) are obtained. It was by this process that the first eurhodine was discovered by Witt in 1883 (Ber. 18, 1119; 19, 441) by heating orthaminoazotoluene with naphthylamine hydrochloride. In this reaction an orthodiamine is formed by the reduction of the amino-azo compound, which combines with α-naphthylamine, hydrogen being eliminated and absorbed by the amino-azo- compound still present.

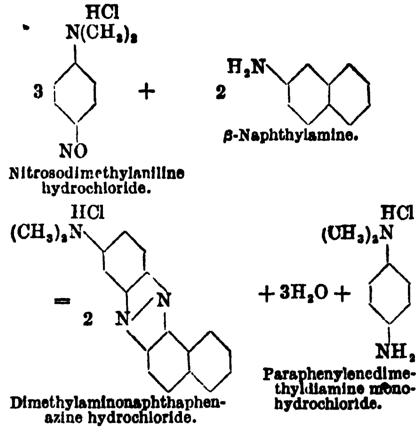
$$C_7H_{10}N_2 + C_{10}H_9N = 6H + C_{17}H_{13}N_3.$$

Orthotolylene-diamine. α-Naphthylamine. Typical eurhodine.

2. Another method of much greater applicability consists in reacting with α-diketones upon aromatic triamines, which contain two amino-groups in the ortho- position. Two molecules of water are eliminated for every molecule of eurhodine formed. Thus, for instance, a eurhodine was obtained from triaminobenzene and phenanthraquinone (Witt, Ber. 19, 445):



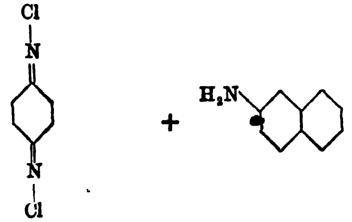
3. Another method of considerable applicability consists in heating together nitroso-amines (Witt, Ber. 21, 719) or quinonedichlorimides (Nietzki a. Otto, Ber. 21, 1598) with aromatic amines in which the para- position to the amino-group is occupied by some radicle. Thus, for instance, a eurhodine is formed by heating together nitrosodimethylaniline hydrochloride and β-naphthylamine, in an acetic acid solution:



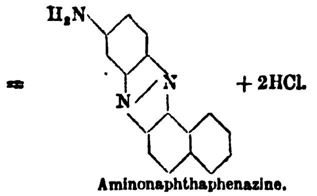
Nitrosodimethylaniline hydrochloride. β-Naphthylamine.

Dimethylaminonaphthaphenazine hydrochloride. Paraphenylenedimethyldiamine monohydrochloride.

and an analogous, though somewhat different reaction takes place if the nitrosodimethylaniline be substituted by dichloroquinonimide.



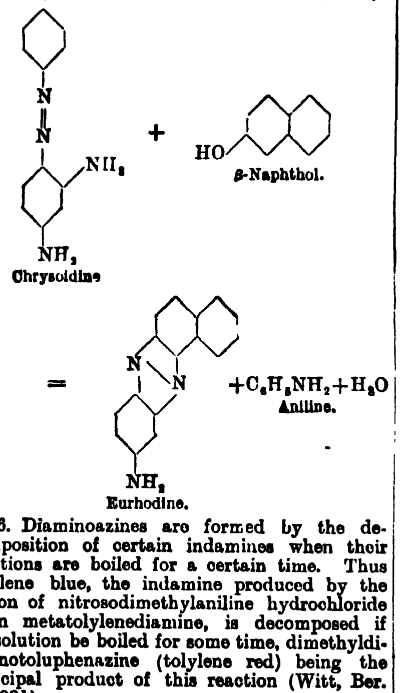
Dichloroquinonimide.



Aminonaphthaphenazine.

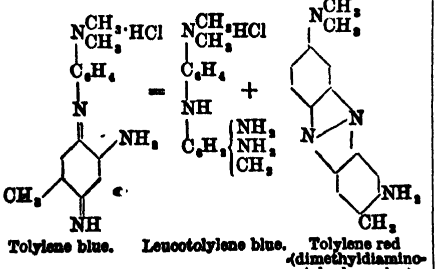
4. Eurhodines proper may also be obtained by the reduction (with ammonium sulphide) of nitro-azines. Thus, for instance, nitrophenophenanthrazine may be reduced into the eurhodine aminophenophenanthrazine (Heim, Ber. 21, 2306).

5. If certain azo- colours, such as chrysoïdine, be heated with β-naphthol, an eurhodine is formed: (Ullmann and Ankersmit, Ber. 38, 1812):



Eurhodine.

6. Diaminoazines are formed by the decomposition of certain indamines when their solutions are boiled for a certain time. Thus tolylene blue, the indamine produced by the action of nitrosodimethylaniline hydrochloride upon metatolylenediamine, is decomposed if its solution be boiled for some time, dimethyldiaminotoluphenazine (tolylene red) being the principal product of this reaction (Witt, Ber. 12, 931):



Tolylene blue. Leucotolylene blue. Tolylene red (dimethyldiaminotoluphenazine).

7. Di- and polyamino- azines may also be prepared by the oxidation of orthodiamines and of polyamines containing two amino- groups in the ortho- position. Thus O. Fischer and E. Hepp proved (Ber. 22, 355) that the red substance which is formed by the oxidation of orthophenylenediamine and which has been observed by many investigators (Griess, Ber. 5, 202; Salkowski, Annalen, 173, 58; Rudolph, Ber. 12, 2211; Wiesinger, Annalen, 224, 353), is nothing else than diaminophenazine. And Nietzki and Müller obtained (Ber. 22, 447) by oxidising tetra-aminobenzene with a current of air tetra-aminophenazine. Aminooxyphenazines may sometimes be found as by-products in this reaction (Ullmann and Mauthner, Ber. 35, 4302 and *ibid.* 36, 4026).

B. Eurhodols.

These may likewise be prepared by various methods.

1. The sulphonic acids of azines, fused with potash, readily yield the corresponding oxyazines or eurhodols (Witt, Ber. 19, 2791). For instance:

$C_{24}H_{13}N_2SO_3Na+2NaOH$
Sodium naphthaphenanthrazinesulphonate.

$=C_{24}H_{13}N_2ONa+Na_2SO_3.$
Phenanthranaphthaeurhodol.

2. Several eurhodines (amino-azines) yield the corresponding eurhodol on being heated under pressure with strong acids, a hydrolysis taking place in the circumstances (Witt, Ber. 19, 444):

$C_{17}H_{11}N_2{\cdot}NH_2+H_2O=NH_3+C_{17}H_{11}N_2{\cdot}OH.$
Typical eurhodine. Eurhodol.

3. Diazo-azines, on being boiled with water, yield the corresponding eurhodols; on being boiled with alcohol they yield the alkyl ethers of these eurhodols (Witt, Ber. 19, 444):

$C_{17}H_{11}N_2{\cdot}N:N{\cdot}Cl+H_2O$
Diazoeurhodine chloride.

$=HCl+N_2+C_{17}H_{11}N_2OH.$
Eurhodol.

$C_{17}H_{11}N_2{\cdot}N:N{\cdot}Cl+C_2H_5OH$
$=HCl+N_2+C_{17}H_{11}N_2OC_2H_5.$
Ethyleurhodol.

The following is an enumeration of those of the eurhodines and eurhodols which have been more closely investigated, the properties of which are typical for the whole class of colouring matters:—

Typical eurhodine $C_{17}H_{13}N_3$ (Witt, Ber. 19, 445). The mode of formation of this substance has already been given (Section A, 1). It is best prepared by heating to 130° equal molecules of orthoaminoazotoluene, of the melting-point 118·5°, and α-naphthylamine hydrochloride, dissolved in phenol until the colour of the mixture, which is at first of an emerald green, has changed into a brilliant scarlet. The mixture is now treated with a large quantity of toluene, when the hydrochloride of the new dyestuff is precipitated in a crystalline state. By recrystallisation from water acidified with hydrochloric acid, it may be obtained in a pure state. From the pure hydrochloride the free eurhodine base is precipitated by alkalis or ammonia in the form of a yellow powder, which may be recrystallised from aniline. Thus prepared, it forms glistening yellow prisms and needles of a dark-brown colour. It dissolves in ether with a yellow colour and a magnificent green fluorescence, which is characteristic of all the members of this group of dyestuffs. Eurhodine forms three series of salts, of which, however, only those with one molecule of acid are fairly stable, whilst those containing more acid are decomposed by the addition of water. It is to the formation of these various salts that the peculiar change of colour is due which is observed on adding water to a solution of eurhodine in concentrated sulphuric acid. This solution is of a cherry-red colour. On adding a small quantity of water the colour changes to a fine emerald green, whilst still more water produces the scarlet shade of the normal sulphate. This change of colour, which is observed with all the eurhodines, links them to their parent-substances, the azines, which exhibit similar curious phenomena, and also to the safranines.

The normal salts of eurhodine are well crystallised and of a bronzed copper colour when solid. In solution they exhibit a bright scarlet tint which they communicate to the fibre. These normal salts are, however, partially decomposed by an excess of water, the free eurhodine base being regenerated. The same takes place if fibres dyed red with eurhodine be washed. The scarlet shade is gradually replaced by the yellow shade of the free eurhodine base. For this reason eurhodine has not found an application in the industry of artificial dyestuffs.

Aminonaphthaphenazine $C_{16}H_{11}N_3$ has been obtained by Nietzki and Otto (Ber. 21, 1598) from β-naphthylamine and dichloroquinonimide (Ullmann and Ankersmit, Ber. 38, 1811). It crystallises in dark-yellow needles. Its salts are of a crimson colour. Its solution in sulphuric acid changes by the addition of water from reddish-brown through green into red. It forms a diazo- compound which, when boiled with alcohol, yields the ordinary naphthaphenazine, of the melting-point 142·5°. The following compound is its dimethyl derivative:—

Dimethylaminonaphthaphenazine $C_{18}H_{15}N_3$ (Witt, Ber. 21, 719). This eurhodine, the formation of which has been described under Section A, 3, may easily be prepared in quantity by heating together 20 parts nitrosodimethylaniline hydrochloride and 10 parts β-naphthylamine with 50 glacial acetic acid; the reaction sets in below 100°, and is apt to become violent. The product changes to a fine violet colour. It is dissolved in water acidified with hydrochloric acid, and the filtered solution is precipitated by the addition of sodium acetate. The crude eurhodine which is thus precipitated may be purified by dissolving it in alcohol acidified with hydrochloric acid. From this solution the normal eurhodine hydrochloride crystallises in bronze-coloured needles. From these ammonia liberates the free eurhodine base in the form of a scarlet crystalline powder. It may be recrystallised from boiling xylene; it is thus obtained in magnificent crystals resembling magnesium-platinocyanide, melting at 205°.

The change of colour of a sulphuric acid solution of this eurhodine is not very marked, going from violet through black and green into violet. The ethereal solution of the free base exhibits the brilliant fluorescence characteristic of all eurhodines.

Aminophenaphenanthrazine $C_{20}H_{13}N_3$. This eurhodine was prepared by Witt (Ber. 19, 445) and by Heim (Ber. 21, 2306) by the methods given under Section A, 2 and 4. It crystallises from toluene in short, thick, yellow prisms, melting at 279°.

Dimethyldiaminotoluphenazine; Tolylene red $C_{15}H_{16}N_4$. The formation of this compound by the spontaneous decomposition of tolylene blue has been described under Section A, 5. This eurhodine forms, in a pure state, orange crystals, which contain 4 mols. of water of crystallisation; at 150° this is given off and the anhydrous base remains as a dark-red powder. The hydrated base is soluble in ether with a pink colour and a beautiful orange fluorescence. The solution in concentrated sulphuric acid is green; on being diluted with water it changes through sky-blue into red. The normal (monacid) salts are perfectly stable and soluble in water with a pink colour. This solution dyes unmordanted or mordanted cotton and other fibres a pink which in darker shades deepens into a coppery red.

The production of this dyestuff has been patented (Otto N. Witt, D. R. P. 15272; Eng. Pat. 4846, 1880). The commercial product, which contains a certain amount of impurities, is sold under the name of 'neutral red.' It is chiefly used in calico-printing, and gives very fast and useful shades.

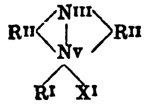
A similar product is prepared from the indamine which is formed by reacting with nitrosodimethylamine hydrochloride upon metaphenylenediamine. It is embraced by the same patent and sold under the name of 'neutral violet.'

Typical eurhodol $C_{17}H_{11}N_2OH$ (Witt, Ber. 19, 444). This substance, the formation of which takes place according to the equation given under Section B, 2, forms small leaflets of a yellow or red colour which dissolve in concentrated sulphuric acid with a red colouration, and are reprecipitated from this solution by the addition of water. Caustic soda solution dissolves it with an orange shade. Thus it is shown that this eurhodol (like all compounds of the same class) exhibits both acid and basic properties, the latter being due to the azine group contained in their molecule.

Eurhodol $C_{24}H_{14}N_2OH$. α-Hydroxynaphthaphenanthrazine has been obtained (Witt, Ber. 19, 2791) by the method described under Section B, 1, by the fusion of naphthaphenanthrazine-α-sulphonic acid with caustic alkalis. Its solution in sulphuric acid is of a fine and intense indigo-blue; it changes very suddenly into red on the addition of water, the sulphate being precipitated. This substance is a yellow colouring matter which may be fixed on cotton with alum-mordant, like alizarin. Owing, however, to its costliness, it has not been brought into commerce. A large number of isomerides may be prepared by starting from the numerous sulpho- derivatives of orthonaphthylenediamine, transforming them into azinesulphonates by condensation with phenanthraquinone and into eurhodols by subsequent fusion with caustic alkalis.

III. **Azonium bases and safranines.** The azonium bases are a class of compounds of which our knowledge is very restricted, very few representatives of the class being at present known, and that rather imperfectly. They are, however, of importance, as it is now established beyond doubt that they are the parent substances of the very important class of dyestuffs known as safranines. Although the first artificial dyestuff, mauveïne, was a true safranine, and although this group of compounds has been frequently under investigation, a correct view of their constitution had not been obtained until quite recently. According to the theory now universally adopted, all safranines are amino- derivatives of azonium bases, to which they stand in the same relation as the eurhodines to the azines. Hydroxy- derivatives of azonium bases have also been prepared and described under the name of safranols. They are, however, of no importance as colouring matters.

The azonium bases themselves, none of which has so far been obtained in a state fit for analysis, stand in the same relation to the azines as the ammonium bases to the amines. They are azines in which one of the nitrogen atoms has become pentavalent by being saturated with three organic radicles and one acid radicle, the connection with the second nitrogen atom being still preserved by the fifth valency of the pentavalent nitrogen atom. Thus the characteristic constitution of the azonium compounds may be expressed by the general formula



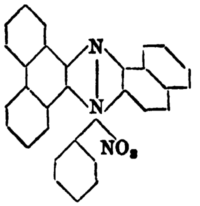
in which R^{I} and R^{II} represent mono- and divalent organic radicles, and X^{I} a monovalent acid radicle. The azonium bases are compounds which possess strong basic properties, and which, by the tenacity with which they retain their acid radicle, strongly resemble the ammonium bases. It is probable that the free azonium bases contain, like the ammonium bases, the hydroxyl group in the position X^{I} of the above general formula. The azonium bases and the dyestuffs derived from them are also capable of tautomeric changes, which lead to their assuming quinonoid structures. The nature of these changes is in many cases doubtful and too complicated to be fully discussed in this article.

The azonium bases are strongly coloured substances, but their dyeing properties are developed and brought to perfection by the introduction of amino- groups into their molecule. As the azonium bases theoretically possible are very numerous, and each of them is capable of producing very numerous isomeric mono- and polyamino- derivatives, the number of possible safranines is exceedingly large, and the number of those which have already been prepared is insignificant in comparison with that foreshadowed by theory.

Of the safranines which have hitherto been prepared, only a few are monoamino- derivatives of azonium bases. A few more are of doubtful or unknown constitution. The majority are asymmetric diamino- derivatives of azonium bases, containing one amino- group in one of the diatomic organic radicles (R^{II}, whilst the other is attached to the monoatomic radicle (R^{I}).

The true constitution of phenosafranine and its congeners has been recognised by Witt, who, after pointing out the analogy between the eurhodines and safranines (Ber. 18, 1119) and clearing up the constitution of the former (Ber. 19, 446), proved the latter to be asymmetric diaminoazonium bases (Ber. 19, 3121). Bernthsen had proposed (Ber. 19, 2690) somewhat earlier a symmetrical formula for the safranines based upon Witt's eurhodine researches. His view was subsequently adopted by some chemists, but the author of this article fails to see the force of the arguments adduced in support of it. *Cf.* supplementary article.

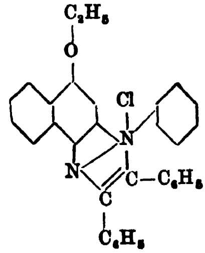
A. Azonium bases. 1. The typical compound was obtained by Witt (Ber. 20, 1183) by the reaction of phenanthraquinone on phenylorthonaphthylenediamine. By heating these ingredients in an acetic acid solution an intermediate product is obtained, which on treatment with a mineral acid is transformed into the salt of the azonium base:



If nitric acid is used, the nitrate is deposited in very fine crystals. It is sparingly soluble in water, readily soluble in spirit with a fine orange-red colouration. The hydrochloride dissolves in sulphuric acid with a violet tint, which changes into red on dilution with water.

2 If in this reaction the phenylorthonaphthylenediamine be replaced by phenylorthophenylenediamine, the resulting compound is a yellow dyestuff of considerable strength. It is manufactured and sold under the name 'Flavinduline' (1893).

3. A very similar compound was obtained by Otto N. Witt and Christoph Schmidt in 1892 (Ber. 25, 1017), by the reaction of benzil upon ethoxyphenylorthonaphthylendiamine. It was called ethoxyphenylnaphthostilbazonium chloride and has the constitution:



It is a beautiful yellow dyestuff, but too expensive to be prepared on a manufacturing scale.

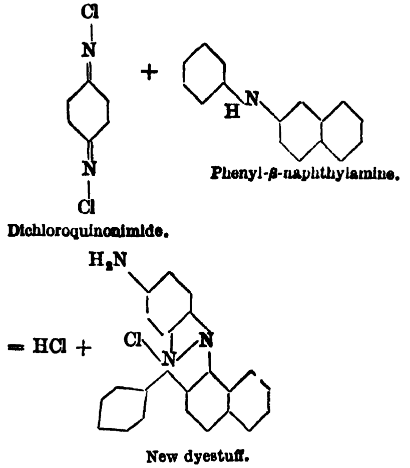
B. Safranines. The various colouring matters belonging to this group have mostly been prepared by different synthetical methods, which may be classed in the following manner:—

1. Reduction of the nitro- derivatives of azonium bases. By reacting with mononitrophenanthraquinone or dinitrophenanthraquinone on phenylorthonaphthylenediamine,

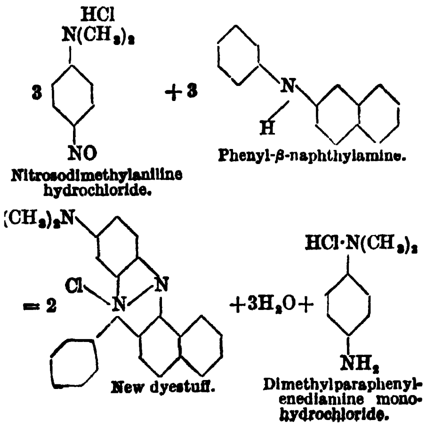
nitro- and dinitro- derivatives of the above azonium base are obtained, which on reduction with ammonium sulphide yield reddish-violet colouring matters belonging to the safranine group (Witt, unpublished observations).

2. If the stilbazonium base obtained by Witt and Schmidt, or any of its congeners prepared from ethylated arylorthonaphthylenediamines be heated with ammonia, the ethoxy group is replaced by the amino- group and the corresponding safranines are formed. This is quite a general reaction (Witt and Schmidt, Ber. 25, 2003; Witt and v. Helmolt, Ber. 27, 2355; Witt and Buntrock, Ber. 27, 2302).

3. By the action of dichloroquinonimides upon secondary aromatic amines, in which the para- position to the amino- group is occupied, monoamino-azonium bases are formed (Nietzki and Otto, Ber. 21, 1598). The reaction, for instance, between dichloroquinonimide and phenyl-β-naphthylamine may be represented by the equation:



4. In a similar manner nitrosodimethylaniline (or any other nitroso-amine) reacts with phenyl-β-naphthylamine (Witt, Ber. 21, 719):

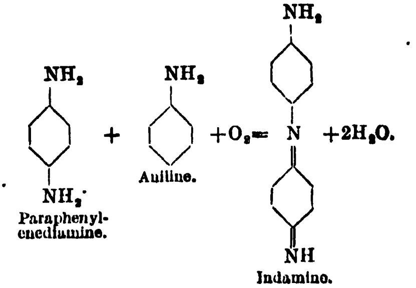


5. The safranines proper (asymmetric diaminoazonium bases) are formed by the joint oxidation of one molecule of diamine and two molecules of an aromatic monoamine. In this reaction fugitive indamines are formed as intermediate products; the process thus becomes strictly analogous to the formation of toluylene red and its congeners.

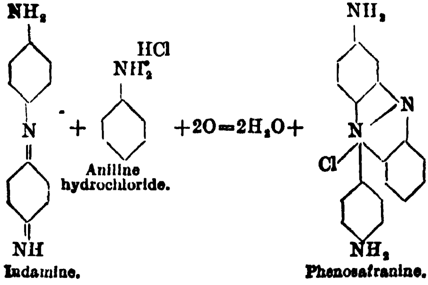
This is the process which is generally used in the manufacture of safranines, and it will therefore be fully explained.

By the joint oxidation of an aromatic paradiamine with one molecule of an aromatic monoamine, an indamine is invariably formed (v. INDAMINES). If these indamines be oxidised in the presence of another molecule of an aromatic monoamine, a safranine is formed:

First Stage.



Second Stage.

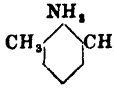


Of course, any other paradiamine may be substituted for paraphenylenediamine, and any other monoamine for aniline. As, however, the formation of an indamine only takes place if the para- position to the amino- group be still free, it results, that at least one of the two molecules of monoamines must fulfil this condition. Thus the formation of a safranine from paraphenylenediamine takes place on oxidation of one molecule of the diamine with

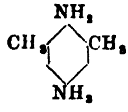
(1) Two molecules of aniline.
(2) Two molecules of orthotoluidine.
(3) One of aniline and one of orthotoluidine.
(4) One of aniline and one of paratoluidine.
(5) One of orthotoluidine and one of paratoluidine; but it does not take place with one molecule of paraphenylenediamine and two of paratoluidine (Witt, J. Soc. Chem. Ind. 1882, 256).

On the other hand, the other of the two

molecules of monoamines must have a free ortho-position in order to be capable of entering the reaction. Thus the indamine of the above formula forms safranines with all the primary aromatic monoamines of the benzene series, with the exception of one xylidine and of mesidine, of the respective formulæ



and

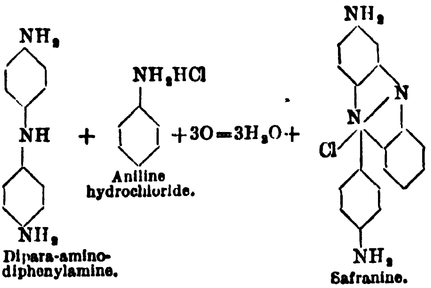


because these two have no free ortho- position to be used for the formation of the azonium group (Nietzki, Ber. 19, 3017 and 3136).

It is also necessary that this second molecule of monoamine be a primary base, whilst the one necessary for the formation of the indamine may be either primary, secondary, or tertiary, provided always that it possesses a free para-position.

6. It is evident that the general process described under 4 may be modified; thus, for instance, the dipara-amino- derivatives of secondary bases (being the leuco- compounds of indamines) may be oxidised together with one molecule of a primary aromatic monoamine, when a safranine is the result (see top of page, second column):

7. Another modification (Witt, Ber. 10, 873) consists in heating aminoazo- compounds with the hydrochlorides of aromatic monoamines.



This is the oldest process for the manufacture of safranines. The mechanism of this reaction is simple. Part of the aminoazo- compound being reduced, a mixture of a paradiamine and a primary monoamine in molecular proportions is formed, which with the monoamine added in the shape of hydrochloride, is transformed into safranine by the dehydrogenating action of the remaining part of the aminoazo- compound. It is evident that the yield must be small in this process of manufacture, and such is actually the case.

8. An asymmetrical safranine has been obtained by the reduction of picryl-orthophenylenediamine (Kehrmann, Ber. 33, 3074).

9. Certain compounds belonging to the safranine group (mauveïne, &c.) are formed in a very complicated reaction by the oxidation of heavy aniline alone; on continued oxidation mauveïne is converted into a safranine (Perkin, Roy. Soc. Proc. 35, 717).

The following is an account of the more important and more thoroughly investigated safranines:—

A. MONAMINO- DERIVATIVES OF AZONIUM BASES.

1. **Aposafranine**, Monoaminophenylphenazonium chloride, has been obtained by Nietzki and Otto (Ber. 21, 1736; *see* also Annalen, 286, 188, and Ber. 30, 2624, and 33, 3078) from phenosafranine (*see* below) by diazotising one of its amino- groups, and eliminating it by means of alcohol. It is a red dyestuff of no practical importance, but very interesting as prototype of the induline group (*see* under INDULINES).

2. **Red dyestuff** $C_{22}H_{16}N_3Cl$. Obtained by the action of dichloroquinonimide on phenyl-β-naphthylamine, was prepared by Nietzki and Otto (Ber. 21, 1598) by heating the ingredients in molecular proportion in alcoholic solution on the water-bath. The nitrate forms green needles or prisms which are soluble in water with a magenta-red colour. The hydrochloride dissolves in sulphuric acid with a red colouration, which on dilution changes through green into red.

3. **Violet colouring matter** $C_{24}H_{20}N_3Cl$. Prepared by Witt (Ber. 21, 719) by acting with 3 molecules of nitrosodimethylaniline hydrochloride in an acetic acid solution on 2 molecules of phenyl-β-naphthylamine. This is the dimethyl- derivative of the preceding substance. The hydrochloride forms large black needles soluble in water, with a fine violet colour. The free base, $C_{24}H_{20}N_3 \cdot OH$, is liberated from the salts by caustic alkalis only. It is insoluble in water, soluble in alcohol, with a red colour and a fine orange fluorescence. It is sold as 'neutral blue.'

4. **Violet colouring matter** $C_{25}H_{22}N_3Cl$. Prepared by Witt (Ber. 21, 719) from paratolyl-β-naphthylamine in exactly the same manner as the preceding substance, of which this is the next homologue. Violet soft needles, resembling in their colour and reactions the phenyl- derivative.

The above substances have been patented (Otto N. Witt, D. R. P. 19224, dated Feb. 18, 1882).

5. **Basle blue** $C_{32}H_{29}N_4Cl$ is a fine blue dyestuff prepared (T. Annaheim, Ber. 20, 1371; Durand and Huguenin, Ger. Pat. 40886) by the reaction of nitrosodimethylaniline hydrochloride on the paratolylnaphthylenediamine which is formed by heating Ebert and Merz's dihydroxynaphthalene with para-toluidine hydrochloride. It forms a brown crystalline powder, soluble in water with a bluish-violet shade. In concentrated sulphuric acid it dissolves with a greenish-brown shade, which changes through green into violet on dilution.

6. **Azine green** $C_{30}H_{25}N_4Cl$ is formed by the reaction of nitrosodimethylaniline hydrochloride upon 2-6-diphenylnaphthylenediamine.

7. **Induline scarlet** $C_{19}H_{18}N_3Cl$, a very beautiful red dyestuff discovered by Schraube (D. R. P. 77266; Eng. Pat. 10138A, 1892), and manufactured by the Badische Aniline und Soda-Fabrik, is really not an induline, but a Safranine. It is prepared by melting together the hydro-

chloride of anilinazoethylparatoluidine and α-naphthylamine. The reaction is strictly analogous to the formation of the typical eurhodine.

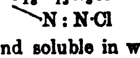
(Induline scarlet is used as a catalyst in discharge printing in some cases (*cf.* D. R. P. 184381). Rongalite special (B. A. S. F.) and hydrosulphite conc. special (M. L. B.) both contain induline scarlet.—F. A. M.)

B. DIAMINO- DERIVATIVES OF AZONIUM BASES.

1. **Phenosafranine** $C_{18}H_{15}N_4Cl$. Discovered by Witt (exhibited in Paris in 1878; and mentioned in the catalogue of Messrs. Williams, Thomas & Dower, closely investigated by Nietzki (Ber. 16, 464) and by Bindschedler (Ber. 13, 207; 16, 865).

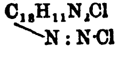
It was with this compound that the mode of formation of the safranines and their chemical properties were definitely ascertained, chiefly by R. Nietzki, whose brilliant researches on this subject did much to clear up the chemistry of this group.

Phenosafranine is prepared by the joint oxidation of paraphenylenediamine and aniline. The mechanism of this process has already been discussed. A dilute aqueous solution of the normal hydrochlorides of these bases is used, and their oxidation is accomplished by adding potassium or sodium bichromate or manganese dioxide in the necessary proportion to the hot solution. The blue colour of the indamine which appears at first is immediately replaced by the red colour of the safranine formed. A certain quantity of insoluble dark by-products is always formed, but by careful work the yield of pure safranine may be raised to 70 p.c. of the theory. When the oxidation is finished, soda solution or chalk is added in order to precipitate the impurities, and the liquid is filtered. By adding a small amount of nitric acid and some sodium nitrate to the filtered solution, the nitrate of the safranine crystallises out; or the chloride may be prepared by adding common salt to the solution after acidifying it with hydrochloric acid. By repeated recrystallisation from water or alcohol, the phenosafranine is obtained in a state of purity, in the form of magnificent green needles. The *sulphate* forms blue needles. The platinum salt $(C_{18}H_{15}N_4Cl)_2PtCl_4$ forms insoluble shining leaflets. Phenosafranine forms a diacetyl- derivative on boiling with acetic anhydride in the presence of dry sodium acetate It forms two diazo-derivatives, of which the first



$$C_{18}H_{13}N_3Cl\diagdown N:N{\cdot}Cl$$

is rather stable and soluble in water, with blue colouration. The other diazo- compound



$$C_{18}H_{11}N_2Cl\begin{cases}N:N{\cdot}Cl\\N:N{\cdot}Cl\end{cases}$$

is very unstable and of a green colour.

Phenosafranine dyes wool, silk, and cotton a magnificent pink. Its aqueous solutions are red and show no fluorescence, whilst alcoholic solutions show a marked greenish-yellow fluorescence. Phenosafranine dissolves in concentrated sulphuric acid with a green colouration which changes through blue into red on dilution, thus indicating the actual existence of the three series of salts foreshadowed by theory.

If phenosafranine or its homologues be diazotised and then combined with β-naphthol, beautiful basic blue dyestuffs are obtained, which are largely prepared and used for cotton-dyeing and calico-printing under the name of 'Indoine blue.'

The alkyl- derivatives of phenosafranine are interesting colouring matters, some of which have found an industrial application. They have not been prepared by introducing alkyl-groups into ready-formed safranine, but rather by direct synthesis from suitable raw materials. Each of them exists in two isomeric modifications, according to the amino- group into which the alkyl- group has been introduced. The two amino- groups of phenosafranine being asymmetric, and therefore not equivalent to one another, must of necessity produce different products on being alkylated.

α-Dimethylsafranine $C_{20}H_{19}N_4Cl$ is produced by the simultaneous oxidation of one molecule of paraphenylenedimethyldiamine with two molecules of aniline.

It is a dyestuff of a magenta-red shade. Its nitrate crystallises in green needles (Bindschedler, Ber. 16, 869).

β-Dimethylsafranine is obtained by oxidising a mixture of one molecule of paraphenylenediamine with one molecule of aniline and one molecule of dimethylaniline. Its shade is similar to that of the preceding one; its nitrate forms brown leaflets (Nietzki, Ber. 19, 3017 and 3136).

The two **diethylsafranines** are obtained in a similar manner. Their chlorides form green needles which dissolve in water with a violet shade (Nietzki, Ber. 16, 464). These substances, and especially the α- derivatives, are manufactured under the name of *Fuchsia*.

Tetramethylsafranine (Bindschedler, *l.c.*) and **tetraethylsafranine** (Nietzki, *l.c.*) may be prepared by the joint oxidation of one molecule of paraphenylenedimethyl- (or diethyl-) diamine with one molecule of aniline and one molecule of dimethyl- or diethylaniline. These substances have been sold under the name of *Amethyst*. Their shade is a magnificent violet, with a fine crimson fluorescence. Unfortunately, they are very fugitive.

2. **Tolusafranines** (Hofmann and Geyger, Ber. 5, 526, and very numerous other publications) $C_{21}H_{21}N_4Cl$. A mixture of the isomerides of this formula is the safranine of commerce. It is prepared by the oxidation of a mixture of paratolylenediamine with the two toluidines. This mixture is obtained by treating three molecules of the orthotoluidine of commerce (which contains from 6 to 10 p.c. of paratoluidine) with two molecules of hydrochloric acid and one molecule of sodium nitrite dissolved in as little water as possible. A thick heavy oil is the result, which is merely a solution of amino-azotoluene in the excess of toluidine present. By dissolving this oil in hydrochloric acid, and reducing it with either zinc-dust or iron borings, the amino-azo- compound is split up into paratolylenediamine and orthotoluidine; consequently, the aqueous liquid produced contains the bases in the necessary proportions for the production of safranine.

The rest of the treatment is exactly similar to) the one described for pheno-safranine. The safranine is precipitated from the liquid by the addition of salt. By redissolving it in water, boiling with a small quantity of potassium bichromate, treating it afresh with milk of lime or chalk, and reprecipitating the filtered liquid with clean salt, the safranine is purified so as to give the brightest shades on dyeing. Safranine prepared with a toluidine rich in paratoluidine is very insoluble in cold water, and therefore generally disliked by the dyer. The presence of aniline has not the same disagreeable effect: some manufacturers therefore use the first runnings of the magenta process, which consist of aniline and orthotoluidine, and contain no paratoluidine, as a suitable raw product for the manufacture of safranine. The safranine of commerce forms a brown powder which dissolves readily in hot water. It dyes a bluish-pink on textile fibres, and was chiefly used for dyeing cotton. The introduction of the so-called substantive azo- colours, derived from benzidine and its congeners, has much diminished the use of safranine.

3. **Girofle.** A dimethylphenoxylosafranine has been produced by heating nitrosodimethylaniline hydrochloride with xylidine, and sold under the above name as a violet colouring matter of a pleasing shade.

4. **Safranisol** $C_{18}H_{13}(OCH_3)_2N_4 \cdot Cl$ is a substance which has been obtained by Nietzki by the joint oxidation of one molecule of paraphenylenediamine with two molecules of ortho-anisidine. It dyes a very beautiful yellowish-pink with a yellow fluorescence. This product has been patented (Kalle & Co., D. R. P. 24229; Eng. Pats. 218, 1883 and 3095, 1883), but owing to the high price of its production it has been unable to compete with the eosin colours, which are perhaps still more brilliant in shade.

5. **Magdala red** $C_{30}H_{21}N_4Cl$. This old and very beautiful colouring matter is the safranine of the naphthalene series. It was discovered by Schiendl and first investigated by Hofmann (Ber. 2, 374), who, however, owing to the great difficulties of its analysis, assigned to it the erroneous formula $C_{30}H_{21}N_3 \cdot HCl$. After a revision of the analytical data by Julius (Ber. 19, 1365), its true composition was established. This substance cannot be prepared by the usual oxidation process from paranaphthylenediamine and naphthylamine because paranaphthylenediamine is at once transformed into α-naphthaquinone even by the feeblest oxidising agents. Magdala red has therefore to be prepared by the old process of heating α-amino-azonaphthalene with α-naphthylamine acetate. The chief product of this reaction is rhodindine, the induline of the naphthalene series (*v.* INDULINES); but a small proportion (6–8 p.c.) of Magdala red is formed at the same time. This is extracted from the melt by repeated treatment with boiling water, in which it is sparingly soluble. On cooling, this solution deposits the dyestuff in the shape of gelatinous flakes, It is purified by repeated crystallisations from water. When pure, it forms a dark crystalline powder, which dissolves in alcohol with a pink colour and a magnificent orange fluorescence. It is used for dyeing light pinks on silk, but is now rapidly being replaced by rhodamine (*v.* TRIPHENYLMETHANE COLOURING MATTERS) If ready-formed paranaphthylenediamine be added to the magenta-melt, the proportion of Magdala red formed is considerably increased (Otto N. Witt, D. R. P. 40868). It is thus shown that Magdala red is, after all, only a product of the joint oxidation of paranaphthylenediamine and α-naphthylamine.

The pure salts of Magdala red, when recrystallised from spirit, form green needles with a metallic lustre. The chloride, sulphate, picrate, and platinum double chloride have been prepared and analysed. These salts dissolve in concentrated sulphuric acid with a blue-black colour which changes into red on dilution.

Mixed Magdala reds have been prepared either by heating amino-azonaphthalene with aromatic monoamines of the benzene series (M. T. Lecco, Ber. 7, 1290), or by heating aminoazo-compounds of the benzene series with paranaphthylenediamine hydrochloride and aniline, toluidine, or even phenol (Otto N. Witt, D. R. P. 40868). These dyestuffs resemble Magdala red in their properties.

6. **Indazine** is the commercial name of a safranine dye, which is obtained by heating the symmetrical diphenylmetaphenylenediamine (prepared by heating resorcin with aniline hydrochloride in the presence of zinc chloride) with nitrosodimethylaniline hydrochloride. Its constitution may be inferred from its analogy to the violet dyestuff prepared from nitrosodimethylaniline and phenyl-β-naphthylamine. It is a serviceable blue, of considerable intensity, but little brilliancy of shade.

Mauveïne $C_{27}H_{25}N_4Cl$. This subtance, the oldest of all the artificial colouring matters, is still manufactured in a small way, and sold under the name of rosolane. It was discovered and examined by W. H. Perkin (Roy. Soc. Proc 35. 717; Eng. Pat. 1984, 1856). who also described the mode of its production. It is prepared by oxidising heavy aniline with potassium dichromate, and extracting the mauveïne formed with water or spirit from the black insoluble mass which is the chief product of the reaction. A dyestuff resembling mauveïne in all its properties may be prepared by the reaction of nitrosodiphenylamine on aniline (Otto Fischer and Hepp, Ber. 21, 2617) or by the joint oxidation of diphenylmetaphenylenediamine and paraphenylenediamine or meta-aminodiphenylamine and para-aminodiphenylamine. These syntheses are a clue to the constitution of mauveïne, which has been a mystery for nearly half a century—it stands revealed as phenylphenosafranine. The above synthetical methods have been adopted for the industrial preparation of mauveïne, as they give better yields than Perkin's old process of oxidation. Mauveïne is generally sold in the shape of a violet paste. It is insoluble in cold, sparingly soluble in hot water, easily soluble with a fine purple shade in spirit. Concentrated sulphuric acid dissolves it with an olive-green colouration, which on dilution with water changes through green and blue into purple. Mauveïne still holds its own against the cheaper new violets on account of its great fastness to light and other influences. It is used for shading the white in bleached silks, and also for printing on paper. (It was also used for printing the old violet penny postage stamp.)

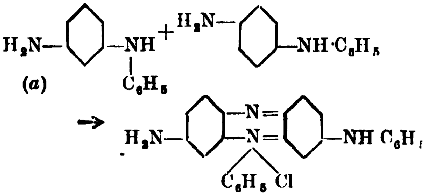
Mauveïne yields on oxidation a pink dyestuff which is supposed to be identical with ordinary phenosafranine. In our opinion this statement requires confirmation. O. N W.

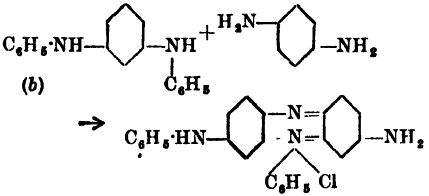
Addendum.

Since the foregoing article was revised by the late Prof. Witt there has been relatively slight activity in the azine group of dyes, such developments as have taken place being chiefly theoretical; on the technical side a few new or improved methods of preparing azine derivatives have been patented, and are noted later, but substantially the situation remains much as it was, no striking advances having been made.

So far as concerns the theory of the structure of the dyes of this class, we may note that the general consensus of opinion amongst chemists is that the ortho-quinoid formulation is, on the whole, in better agreement with the known facts than the older para-quinoid structures ascribed to them by Witt, and, in addition, safranine, one of the most important members of the azine series, is usually given a symmetrical formula rather than the unsymmetrical formula favoured by Witt.

We may therefore note shortly the chief grounds upon which these alterations are based: first as regards the symmetrical formulation, Nietzki showed that the same phenyl-safranine was obtained by condensing (*a*) phenyl-*m*-phenylenediamine and phenyl-*p*-phenylenediamine; (*b*) diphenyl-*m*-phenylenediamine and *p*-phenylenediamine, according to the schemes:


(*a*)

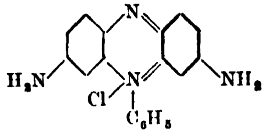

(*b*)

A result that appears hardly explicable if we assume a symmetrical formula for the safranine.

Further, the synthesis of safranine from *m*-aminodiphenylamine and *p*-phenylenediamine also points in the same direction, since a safranine is also produced if methyl-*m*-phenylenediamine be used in place of phenyl-*m*-phenylenediamine, a result clearly incompatible with an unsymmetrical formula, for whilst the methyl group can replace the phenyl group attached to the azonium nitrogen on the symmetrical formula, it cannot possibly replace one of the benzene nuclei of the azine ring system as would be demanded by the unsymmetrical formula.

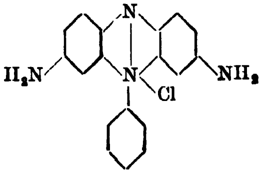
Nietzki claimed to have shown the existence of two isomeric diethyl safranines which he prepared from diethylphenylenediamine + 2 mols. aniline, and from aniline, + *p*-phenylenediamine + diethylaniline respectively, and quoted this as an argument in favour of the unsymmetrical formula. Körner and Schraube, however (Chem. Zeit. 17, 305), destroyed this argument by showing that the two isomers were identical. A further argument in favour of the unsymmetrical formula was brought forward by Barbier and Sisley (Ann. Chim. Phys. 1908, 96), who claimed to have proved the existence of two isomeric safranines, an unsymmetrical and a symmetrical, the technical dye consisting of a mixture of both forms. Hewitt, Newman, and Winmill have, however, contradicted this statement (Chem. Soc. Trans. 1909, 95, 577). Havas and Bernhard (Ber. 46, 2723) also claim to have proved that phenosafranine is homogeneous, and that Barbier and Sisley's two products are either different hydrates or homologues which may be present in the purest commercial safranine.

The balance of evidence appears, therefore, to be strongly in favour of the symmetrical formula for the safranines:

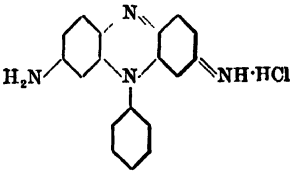


As regards the vexed question of *ortho-* versus *para-* quinoid structure, we cannot say that this is finally settled, as there is little doubt that, in certain cases, at all events, tautomerism occurs between the two forms.

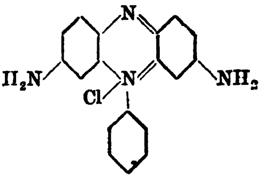
Assuming the correctness of the symmetrical arrangement discussed above, we have three possible methods of writing the structural formula:—



I.



II.

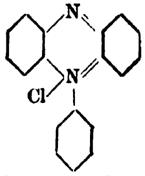


III.

(For a fourth suggested formula, *cf.* Balls, Hewitt, and Winmill, Chem. Soc. Trans. 1912, 101, 1840.)

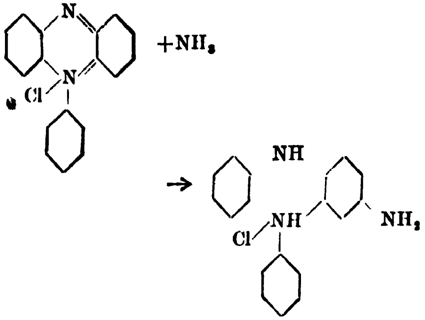
Of these, formula I., originally proposed by Bernthsen (Ber. 19, 2690), is constructed in accordance with the older 'peroxide' formula for quinone, which is not used now, and may therefore be disregarded.

Between II. and III., the *para*-quinoid and the *ortho*-quinoid formulæ, a decision could be arrived at by the behaviour of the substance with nitrous acid, since II. contains only one amino- group, whilst III. possesses two. One amino- group can be readily removed by diazotisation in the ordinary way, yielding aposafranine, whilst the second group is considerably more resistant; but Kehrmann (Ber. 1896, 29, 2316), by diazotising the sulphuric acid solution of aposafranine, succeeded in removing the second amino- group, obtaining by this means phenyl phenazonium chloride :

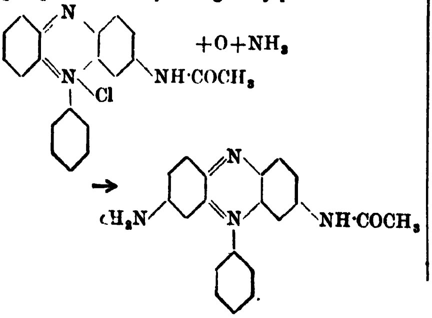


which can only have an *ortho*-quinoid structure (*cf.* also Nietzki, Ber. 29, 2771).

A further proof by Kehrmann (Ber. 30, 1565, 2620; 33, 395) consists in the fact that on treating phenylphenazonium chloride with ammonia an amino- group is added on (just as quinone, for example, adds on hydrochloric acid) yielding leucoaposafranine :



which oxidises at once in air to aposafranine itself; if the latter be then acetylated and again treated with ammonia a further amino- group is added on yielding acetylphenosafranine :



Such a synthesis is readily explicable on the *ortho*-quinoid hypothesis, but it would be difficult to understand how ammonia could add on to the non-quinoid nucleus were the *para*-quinoid structure accepted.

We may therefore take it that the behaviour of the azine group of dyes can be best explained by the assumption of an *ortho*-quinoid structure, but the possibility of tautomeric change into the *p*-quinoid form must not be lost sight of.

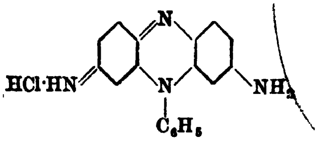
Kehrmann, Havas, and Grandmougin, and their pupils, have carried out a good deal of research in recent years on the structure of the azine dyes. In particular, they have examined the behaviour of some phenazonium compounds with varying concentrations of sulphuric acid. As is well known, by increasing the concentration of the acid striking colour changes are produced, and the results obtained show that, with few exceptions, the number of colour changes produced increases with the number of amino- groups present in the molecule, which they explain by assuming that salt formation takes place step-wise, each transformation of a basic into a salt group causing a colour change.

Frequently the second salt of a diamino compound exhibits colour and spectral relationships identical with those shown by the salt of the monoamino compound, the effect of the acid being to neutralise the chromophoric effects of the particular amino- group, *e.g.* the 'second' colouration of 1 : 3, 3 : 7, or 3 : 11 diaminophenylphenazonium salts is the same as that of the 3-amino- compound 'first' colouration (Ber. 46, 2802).

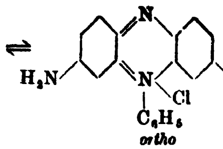
Where this rule does not hold good the assumption is made that a change has occurred from *ortho*- to *para*-quinoid structure, or *vice versa*.

Most of the researches of these investigators are of too theoretical a nature to be considered in the present article, but it is worthy of note that they bring forward evidence which tends to show that the assumption of such a change in the structure of azine dyes from *ortho*- to *para*-quinoid rests to some extent on an experimental basis. Thus Grandmougin and Smirous (Ber. 46, 3425) consider that the green tri-acid safranine salts obtained on solution in sulphuric acid are mixtures of a yellow *o*-quinoid, and a blue *p*-quinoid compound, and it was found that on treating such green solutions with sodium nitrite they at first undergo only partial diazotisation, but on standing for some days the *para*- form is slowly rearranged into the ortho-quinoid form, and is bis-diazotised so that on pouring into alcohol phenylphenazine is formed.

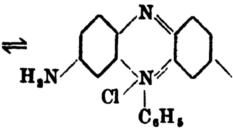
Balls, Hewitt, and Newman (Chem. Soc. Trans. 1912, 101, 1840), from an examination of the absorption curves of various azine dyes, consider these to confirm the tautomeric structure of the safranines, the structure changing from *ortho*- to *para*-quinoid, according to conditions :



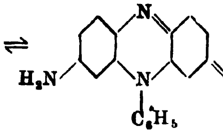
para



ortho



ortho

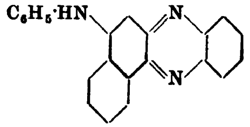


para

Regarding other recent developments we may note that phenazine has been produced by Zerevitinov and Osstromuisslenski (Ber. 44, 2402) by heating nitrobenzene with barium oxide at 200°–280° C., the only other substance produced being aniline.

Another synthesis from *o*-nitraniline and *o*-nitrobrombenzene, using cuprous chloride as a catalyst, is described by Eckert and Steiner (Monatsh. 1914, 35, 1153).

On the purely technical side we may note that Bayer & Co. (D. R. P. 230456) describes the production of green azine dyes of the type:



from 1 : 3-diarylnaphthylene diamines or their sulphonic acids. By oxidising alkylbenzyl-aniline sulphonic acids with derivatives of diphenylamine sulphonic acids of the general formula:

$$(H_2N)\cdot(SO_3H):C_6H_3\cdot NH\cdot C_6H_4\cdot X$$

(X=hydrogen or aralkyl)

to the corresponding indamine, and then the latter with an aromatic amine, safranine sulphonic acids are produced (Akt. ges. f. Aniline Fab.; Fr. Pat. 417669).

In Fr. Pat. 426790 (D. R. P. 243491) the Farbwerke Höchst claim the production of a safranine disulphonic acid by the joint oxidation of *p*-iminodiphenylamine sulphonic acids, sulphanilic acid, and monosulphonic acids of tertiary amines in which the *para*- position is free, such as alkyl-benzyl-aniline sulphonic acids.

J. D. Riedel claims the manufacture of azine dyes by the action of *m*-toluylene diamine and *α*-naphthylamine upon *p*-nitroso phenylglycine (Eng. Pat. 22694, 1913; D. R. P. 268208).

Basic safranine dyes result from the condensation of nitrosomethyl-*o*-toluidine and *m*-aminomethyl-*p*-toluidine, giving yellowish-red prints on cotton. A better method is to produce these safranine dyes by oxidising a mixture of methyl-*p*-toluylenediamine and methyl-*m*-toluylenediamine (Durand, Huguenin & Co., Eng. Pat. 2933, 1915; D. R. P. 282346, 287271).

Bayer & Co. claim the production of compounds of basic dyes of the safranine series by converting the dyes or their salts into the corresponding gallocarboxylic acid salts (D. R. P. 285500).

A somewhat fresh application of safranines is given by the Saccharin Fabrik vorm. Fahlberg List & Co., who claim the treatment of phenosafranine and its homologues with mercury salts, the resultant mercurised safranines possessing therapeutic properties (D. R. P 286097).

Another therapeutic use for safranine derivatives is described by the Akt. Ges. f. Aniline Fab. (Fr. Pat. 463357), who claim the preparation of a substance by combining tolusafranine with tannin in hot 8 p.c. soda lye, and precipitating the product with salt; it forms a red powder slightly soluble in water, soluble in concentrated sulphuric acid to a green solution. It has no purgative action, and may be used as a drug for the treatment of trypanosoma and other protozoic infections.

Finally, it should be noted that recent work by Green and others (Ber. 44, 2570; 45, 1955; 46, 33; Proc. Chem. Soc. 28, 250, 1912; Chem. Soc. Trans. 97, 2388) has proved that aniline black is a complex azine derivative (*see* ANILINE BLACK). The indulines and nigrosines are also complex derivatives containing azine nuclei (*see* INDULINES and NIGROSINES).

F. A. M.

AZOBENZENE $C_{12}H_{10}N_2$. A product of the partial reduction of nitrobenzene, obtained by Mitscherlich (Annalen, 12, 311) by boiling an alcoholic solution of nitrobenzene with potash and distilling the product.

Preparation.—Azobenzene is obtained by acting with sodium amalgam (4–5 p.c. of sodium) on nitrobenzene dissolved in ether containing water (Werigo, Annalen, 135, 176; Alexejeff, J. 1864, 525; Rasenack, Ber. 5, 367); the product, according to Alexejeff (J. 1867, 503) is azobenzene or azoxybenzene, according as the sodium amalgam or nitrobenzene is in excess. On the large scale azobenzene is prepared by the reduction of nitrobenzene in alcoholic solution with zinc-dust and aqueous soda. In this reaction the reduction tends to go further, and some hydrazobenzene is also obtained; this, however, is readily oxidised to azobenzene if nitrous fumes are passed into the alcoholic solution of the product (Alexejeff, J. 1867, 503). Azobenzene can also be prepared by distilling azoxybenzene (1 part) with iron filings (3 parts) (Schmidt and Schultz, Ber. 12, 484); by heating nitrobenzene on a water-bath with the calculated quantity (2 mols.) of stannous chloride dissolved in excess of aqueous caustic soda (Witt, Ber. 18, 2912); by reducing nitrobenzene in alcoholic solution with magnesium amalgam (yield 95 p.c.) (Evans and Fetsch, J. Amer. Chem. Soc. 1904, 1158); by reducing nitrobenzene with alkali sulphide in the presence of alkali (Farb. vorm. Meister, Lucius, and Brüning, D. R. P. 216246, J. Soc. Chem. Ind. 1909, 1310); by heating nitrobenzene with charcoal and alkali (Farb. vorm. Fried. Bayer & Co., D. R. P. 210806; Chem. Zentr. 1909, 2, 163); by treating phenylhydrazine with bleaching powder solution (Brunner and Pelet, Ber. 1897, 284). Azobenzene can be prepared by the electrolytic reduction of nitrobenzene in the presence of alkali (Elbs and Kopp, J. Soc. Chem. Ind. 1898, 1137; Löb, Ber. 1900, 2329; Farb. vorm. Fried. Bayer & Co., D. R. PP. 121899 and 121900; Chem. Zentr. 1901, 2, 153; Farb. vorm. Meister, Lucius and Brüning; D. R. P. 141535; Chem. Zentr. 1903, (i.) 1283; and Farb. vorm. Weiler-ter-Meer, D. R. P. 138496; Chem. Zentr. 1903, (i.) 372).

Properties.—Azobenzene crystallises in large yellowish-red crystals belonging to the monoclinic system (Boeris, R. Accad. Lincei, [5] 8, i. 575), and to the rhombic system (Alexejeff, Chem. Soc. Abstr. 42, 965); melts at 68°, boils at 293°, and is readily soluble in alcohol and ether, insoluble in water. From benzene it crystallises with benzene of crystallisation in rhombic prisms, which lose benzene on exposure to the air. Weak reducing agents, such as ammonium sulphide or zinc-dust in alkaline solution (Alexejeff, Annalen, 207, 327) or phenylhydrazine (Walther, J. pr. Chem. 1896, 54, 433), convert azobenzene into hydrazobenzene, but benzidine is obtained when stronger reducing agents such as sulphurous acid or hydrogen iodide are employed (Bordenstein, D. R. P. 172569; J. Soc. Chem. Ind. 1907, 272), or the alcoholic solution is treated in the cold with stannous chloride and a little sulphuric acid (Schultz, Ber. 17, 464; Mentha and Heumann, Ber. 19, 2970). Azobenzene can also be electrolytically reduced to benzidine (Löb, Ber. 1900, 2329; when heated with ammonium hydrogen sulphite and alcohol under pressure, it is converted into benzidinesulphamic acid (Spiegel, Ber. 18, 1481). When melted with *p*-phenylenediamine in the presence of ammonium chloride, it yields a soluble induline dye (Farb. vorm. Fried. Bayer & Co., D. R. P. 53198; Ber. 1891, Ref. 137). Azobenzene yields a mixture of mono-, di-, and trinitroazobenzenes when treated with fuming nitric acid (Gerhardt and Laurent, Annalen, 75, 73; Janovsky and Erb, Ber. 18, 1133; 19, 2157; Janovsky, Monatsh. 7, 124; Werner and Stiasny, Ber. 1899, 3256): ordinary sulphuric acid dissolves it without alteration, whilst the fuming acid at 130° converts it into azobenzenemonosulphonic acid (Griess, Annalen, 154, 208; Janovsky, Monatsh. 2, 219); chromic acid oxidises it to carbon dioxide and nitrogen (De Coninck, Compt. rend. 1899, 128, 682). The bromine derivatives of azobenzene have been examined by Werigo (Annalen, 165, 189), Janovsky (*l.c.*), and Mills (Chem. Soc. Trans. 1894, 51).

AZOBENZENE RED *v.* Azo- colouring matters.

AZO-BLACK or **NAPHTHOL BLACK** *v.* Azo- colouring matters.

AZO-BLUE *v.* Azo- colouring matters.

AZO-COCCINE *v.* Azo- colouring matters.

AZO- COLOURING MATTERS.

History.—The colouring matters of this class contain one or more azo-groups —N : N— linking together aromatic radicals. The typical parent substance from which these compounds may be regarded as being derived is azobenzene. $C_6H_5{\cdot}N:N{\cdot}C_6H_5$, which has been known since the year 1834 (Mitscherlich, Annalen, 12, 311). The basic and acid derivatives of azobenzene are all colouring matters, the amino- derivative, aminoazobenzene, having been the first of these compounds which was prepared and introduced into commerce on anything approaching a large scale by the firm of Simpson, Maule, and Nicholson in 1863. This substance was prepared by the action of nitrous gases on aniline dissolved in alcohol, and was known in the market by the name of 'aniline yellow,' the true constitution of the colour being at the time unknown. The introduction of the first azo-colour into commerce is thus due to the firm above mentioned, although the production of the colour itself appears to have been previously observed by Mène (Compt. rend. 1861, 52, 311), Luthringer (Fr. Pat. 50901, Aug. 30, 1861), and Griess (Annalen, 1862, 121, 262, *note*). The first researches on the diazo- compounds (as distinguished from azo- compounds) were published in 1858 by Griess (Annalen, 106, 123), who in 1862 discovered a compound produced by the action of nitrous acid on aniline, to which he gave the name of 'diazoamidobenzol' (Annalen, 131, 257). The latter was, however, a true diazo- compound, and on comparing it with the 'aniline yellow' of commerce it was found that the two substances were isomeric, a discovery which led to the establishment of the true formula of aminoazobenzene by Martius and Griess in 1866 (Zeitsch. Chem. N. F. 2, 132). In this same year a brown dye was sent into the market by the firm of Roberts, Dale, and Co., of Manchester, and this colouring matter (known as Manchester Brown, Vesuvine, Phenylene Brown, or, more generally, Bismarck Brown) was investigated by Caro and Griess, and identified as an azo- compound in 1867 (Zeitsch. Chem. N. F. 3, 278). These chemists regarded it as triaminoazobenzene, but G. Schultz (Chemie des Steinkohlentheers, 2nd ed. 2, 193) showed that it is benzene-1 : 3-disazophenylenediamine. This compound still occupies an important place in the tinctorial industries, whilst the earlier known aminoazobenzene (aniline yellow) has been completely abandoned on account of its fugitive character. It is, however, used in the preparation of other azo-colouring matters and indulines. In 1876 a beautifully crystalline orange colouring matter made its appearance as a commercial product under the name of 'chrysoïdine,' its composition and constitution having been established by Hofmann (Ber. 1877, 10, 213), who showed that it was diaminoazobenzene. This colouring matter was discovered almost simultaneously by Caro and Witt, independently, in 1876, but was first introduced into commerce by the latter, the manufacture having been carried out by the firm of Williams, Thomas, and Dower, o Brentford and Fulham.

The manufacture of chrysoïdine was the first industrial application of Griess's discovery of the diazo- compounds, the colouring matter in question being prepared by the action of a diazo-salt (diazobenzene chloride) on *m*-phenylenediamine, and this manufacture was soon followed by the appearance of acid azo- compounds prepared by the action of diazosulphonic acids on phenols. The typical parent substance of these acid azo- colours may be regarded as hydroxyazobenzene, $C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}OH$, which was first prepared by Griess in 1864 (Phil. Trans. 153, 679). The general method by which the azo-colours are now prepared is an application of the reaction between diazo- salts and phenols in alkaline solution, first made known by Kekulé and Hidegh (Ber. 1870, 3, 233), the first colouring matters of this class having been introduced by Witt under the name of 'Tropæolines' (Chem. Soc. Trans. 1879, 35, 179), and simultaneously by Poirrier, of St. Denis, under the designation of 'Orange' of various brands. Since the first appearance of the acid azo- colours immense numbers of these compounds have been sent into commerce under various designations, the first patent having been taken out by Griess in 1877 (E. P. 3698), and being quickly followed by others, which will be referred to in due order. Of the acid azo- colours described in the earlier specifications, the most successful from an industrial point of view were those manufactured by the Badische Anilin- und Soda-Fabrik (Ber. 1879, 12, 1364), and by Meister, Lucius, and Brüning, of Höchst (*ibid.* 144).

The next step of importance in the industrial history of the azo- colours was the introduction of *disazo- compounds*, containing two azo- groups. The typical compound of this class is benzeneazobenzeneazophenol $C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}OH$, discovered in 1877 by Caro and Schraube (Ber. 10, 2230). In 1879 appeared the 'Biebrich scarlet' of Nietzki (Ber. 1880, 13, 800, 1838), which was introduced by the firm of Kalle & Co. of Biebrich. This dyestuff is prepared by combining diazotised aminoazobenzenedisulphonic acid with β-naphthol, and was the first of the *secondary* disazo- compounds. The first *primary* disazo- colouring matter, 'Resorcin brown,' was discovered in 1881 by Wallach, who combined *two* molecules of a diazo- compound (m-xylidine and sulphanilic acid) with *one* molecule of a phenol (resorcinol). In 1884 a very important discovery in the history of azo-colouring matters was made by P. Böttiger, who found that the disazo- compound obtained by combining the tetrazo- salt prepared from benzidine with naphthionic acid possessed the valuable property of dyeing cotton direct, without the use of a mordant. This colouring matter was put on the market by the Aktiengesellschaft für Anilinfabrikation, under the name of 'Congo red.' This discovery has given rise to the production of a very large number of similarly constituted colouring matters, which appear on the market under the names of benzo-, Congo-, diamine-, and other dyestuffs. In the following year another important development was announced by the introduction of the first satisfactory black azo- colouring matter (naphthol black) for wool. This was discovered by Hoffmann and Weinberg, and placed on the market by L. Cassella & Co. In 1887 A. G. Green found that primuline, which he had discovered, dyed cotton direct, and that the yellow colouring matter when thus dyed on the fibre, could be diazotised and combined (developed) with β-naphthol, m-phenylenediamine, and similar 'developers,' thus giving rise to a series of new azo- dyestuffs (Ingrain colours). This discovery led to the manufacture of many azo-colouring matters which were capable of being similarly diazotised and developed on the fibre (*e.g.* diamine black), as also to the production of azo- colouring matters on the fibre by treating the fibre already dyed with an azo- colour with a diazo- compound (*e.g.* benzonitrol colours). In both cases darker and faster dyeings are obtained.

The first direct cotton black (diamine black, RO) was discovered in 1889 by Gans (Cassella & Co.), and in 1891 Hoffmann and Daimler prepared the first green colouring matter of this kind (diamine green).

A modified method of the process introduced in 1880 by Read Holliday and Sons, of producing insoluble azo- colouring matters directly on the fibre, has been largely developed of late years. The first example of this, viz. the combination of diazotised p-nitroaniline with β-naphthol ('paranitraniline red') still holds the place of greatest importance.

Manufacture.—The general method of preparing the azo- colours on a large scale depends upon the reaction between a diazo- salt, usually the chloride, and a phenol or phenolsulphonic acid in presence of an alkali, as typified by the following example :—

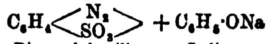
$C_6H_5{\cdot}N_2Cl+C_6H_5{\cdot}ONa$

Diazobenzene chloride. Sodium phenoxide.

$=C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}OH+NaCl.$

Benzeneazophenol.

Aminosulphonic acids or aminocarboxylic acids when diazotised react in a similar manner :



$$C_6H_4\left\langle\begin{matrix}N_2\\SO_3\end{matrix}\right\rangle + C_6H_5{\cdot}ONa$$

Diazosulphanilic acid. Sodium phenoxide.

$=SO_3Na{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}OH.$

Sulphobenzeneazophenol (sodium salt).

Preparation of the diazo- salts.—The amine to be diazotised is usually dissolved in about 10 parts of water and one equivalent of hydrochloric (more rarely sulphuric) acid. For diamines twice this amount of acid is taken. The solution[1] is now cooled by adding ice until the temperature is, in the case of aniline, the toluidines, the xylidines, &c., 0°–2°, or, in the case of the naphthylamines, the nitroanilines and diamines such as benzidine, tolidine, dianisidine, &c., 5°–10°. This is done by adding ice to the solution. More acid (1½–2 equivalents) is now added (or 3–4 in the case of diamines), and a solution of the calculated quantity of sodium nitrite is run in, sufficient being used to give a reaction with starch-iodide paper after the whole has been mixed for two or three minutes. (For velocity of diazotisation, *see* Hantzsch and Schumann, Ber. 1899, 32, 1691 ; Schumann, *ibid.* 1900, 33, 527 ; Tassilly, Compt. rend. 1913, 157, 1148 ; 1914, 158, 335, 489). In certain cases (*e.g.* α-naphthylamine, p-nitroaniline, &c.) it is better to add the nitrite all at once in order to avoid the formation of the diazoamino- compound. In diazotising such compounds as give an insoluble diazo-derivative, as, for example, *p*-sulphobenzeneazo-*a*-naphthylamine or *p*-acetylaminobenzeneazo-*a*-naphthylamine, and which themselves are insoluble in acids (under the above conditions) it is advisable to use an excess of nitrite and to stir the ice-cold mixture for several hours. Special methods have to be employed to diazotise amines containing several negative groups; the operation may often be effected by carrying it out in the presence of excess of 50 p.c. sulphuric acid, and Witt has shown (Ber. 1909, 42, 2953) that diazotisation is easily brought about in these cases by employing strong nitric acid. Other substances which are difficult to diazotise satisfactorily are those which are readily oxidised by the nitrous acid, such as the 1 : 2- and the 2 : 1-aminonaphthols and their sulphonic acids. In this case the diazotisation may be done in the presence of zinc or copper salts (compare E. P. 10235 of 1904; D. R. P. 171024, 172446; F. P. 353786) or by means of zinc nitrite. Another method is to diazotise in presence of an excess of acetic or oxalic acid (compare D. R. P. 155083, 175593, also E. P. 2946 of 1896).

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[1] Some of the diazosulphonic acids, such as diazonaphthionic acid, are insoluble in water, and are therefore employed in a state of suspension.

Difficulties are often encountered in endeavouring to diazotise certain diamines. *o*-Phenylene- and tolylene-diamines cannot be diazotised, as they yield the azimino- derivatives, and, under the usual conditions, the meta-diamines furnish Bismarck brown; but if the diamine is run into a mixture of nitrite and acid the tetrazo-compound may be obtained (Griess, Ber. 1886, 19, 317; Täuber and Walder, Ber. 1897, 30, 2901; E. P. 1593 of 1888; D. R. P. 103685). In the case of *p*-phenylenediamine and certain diamines of the naphthalene series diazotisation is brought about indirectly, as the direct action of nitrous acid often leads to a mixture of the mono- with the bis-diazo- (or tetrazo-) compound. Either the corresponding nitroamine or the monoacetylated diamine is employed. This is diazotised and combined with a component in the usual way (*see* below), and then the nitro-group is reduced or the acetyl group hydrolysed when the free amino- group can then readily be diazotised. Some diamines, indeed, can only be diazotised as regards one amino-group, the other being quite unattacked. In such cases (*e.g.* *o*-nitro-*p*-phenylenediamine, 1 : 4-naphthylenediamine-2-sulphonic acid—the latter being diazotisable only in acetic or oxalic acid solution) the monodiazo-salt is combined with a component and then the remaining amino- group, which before resisted all attempts at diazotisation, is easily diazotised (compare Bülow, Ber. 1896 29, 2285; E. P. 2946 of 1896). (For further information on this subject, see Cain, The Chemistry and Technology of the Diazo- Compounds, Arnold, 1920.)

Combination (coupling) of the diazo- compound with a component (phenol or amine) to form an azo- dyestuff.[1]—Before the diazo- solution is prepared a solution of a phenol or amine is made ready so that no delay may occur before coupling takes place. As a general rule, phenols are combined in alkaline and amines in acid (acetic) solution. In the case of phenols or naphthols the substance is first dissolved in the calculated amount of sodium hydroxide, the solution diluted with water, and sodium carbonate added in sufficient quantity to ensure an alkaline reaction being obtained at the end of the combination (*i.e.* a little more than one molecule of sodium carbonate to each molecule of hydrochloric acid, so that sodium hydrogen carbonate may be formed). When phenolic sulphonic acids are the components, they may be dissolved in sodium carbonate instead of hydroxide. The phenolic solution, having been cooled to about 10°, is now ready, and the diazo- solution is run in gradually with constant stirring. Combination takes place at once,[1] and when all the diazo- solution has been added, the mixture must be tested to ensure an alkaline reaction, and the presence of a slight excess of the phenol (about 2–5 p.c. excess of the theoretical amount is usually taken). The next day the colouring matter is filtered through filter presses. If it has separated out, no further treatment is necessary, but if it is still partly or wholly in solution, it is 'salted out' (hot or cold) by adding common salt until a spot on filter paper shows only a faintly coloured rim. In rare cases the precipitation is effected by acidifying. The filtration is best effected by the aid of compressed air and the press cake is spread on trays and dried. The dry lumps are then ground in a mill, adjusted to 'type' or 'standard' by means of common salt, sodium sulphate, &c., and the product is then ready for the market. In cases where the possibility of the formation of a disazo- dyestuff is present (dihydroxy- compounds, *a*-naphthol, &c.), the coupling may advantageously be carried out in acetic acid solution.

The procedure adopted in the case of amines is very similar to the above. The amine is first dissolved in the appropriate amount of hydrochloric acid, the solution diluted and sufficient sodium acetate added to ensure that no free mineral acid remains at the end of the combination (in rare cases coupling is effected in mineral acid or alkaline solution). When the combination is complete, the dyestuff is filtered off either as it is or after having been rendered alkaline.

Many disazo- dyestuffs are prepared by combining two molecules of the same or different diazo- compounds with an aminonaphtholsulphonic acid. In this case combination is effected first in acid solution and then the monoazo- dyestuff thus formed is rendered alkaline, and the second molecule of diazo-compound added.

Position assumed by the azo- group in the formation of azo- colouring matters.—(*a*) *Benzene series*: When the para- position with respect to the amino- or hydroxy- group is occupied by a hydrogen atom, and no group, such as NO_2, SO_3H, or NR_3Cl, is in the meta- position, the azo- group enters the para- position in place of the hydrogen atom. (*b*) *Naphthalene series*: In corresponding compounds of the naphthalene series (*a*-naphthylamine, *a*-naphthol) the entering azo- group also takes up the para- position, but when, in *a*-naphthol, a sulphonic group is in the 3- or 5-position with respect to the hydroxy- group, or a nitro- or NR_3Cl- group is in the 3- position the azo- group enters the 2- position.

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[1] For the mechanism of the reaction, *see* Charrier Gazz. chim. ital. 1914, 44, ii. 503; Auwers and Michaelis, Ber. 1914, 47, 1275; Meyer, Irschick and Schlösser, *ibid.* 1741; and Karrer Ber. 1915, 48, 1398.

[1] For the formation of diazo-oxy- compounds, *see* a paper by Dimroth and Hartmann, Ber. 1908, 41, 4012.

When the para- position is substituted, the azo- group enters the ortho-(2)- position, but if the para- substituent is a carboxy- group, this is usually displaced by the azo- group.

When diazo- compounds act on β-naphthylamine or β-naphthol. the azo- group enters position 1 (in the ortho- position with respect to the amino- or hydroxy- group). If the 1- position in β-naphthol is occupied by a carboxy- group, this is displaced (compare also Scharwin and Kaljanoff, Ber. 1908, 41, 2056 and article on DISAZO- and TETRAZO- COLOURING MATTERS).

Differing capacity for combination.—As will have been gathered from the preceding paragraph, the azo- group never enters the meta- position with respect to an amino- or hydroxy- group. Further, a component in which the para- position is occupied by a substituent group is not so readily attacked (in the ortho- position) as one that is not substituted (when the azo- group enters the para- position). Moreover, the capacity for combination depends also on the kind of diazo- compound employed, thus 2-naphthol-8-sulphonic acid and 2-naphthol-6 : 8-disulphonic acid in dilute solution do not combine at all with diazotised xylidine or naphthylamine, whilst diazotised aniline, aminoazobenzene, aminoazobenzenesulphonic acid and naphthylaminesulphonic acids couple easily with them. The combination with diazotised xylidine and naphthylamine can, however, be made to take place in concentrated solution. The diazo- compound of *p*-nitroaniline, in most cases, combines with extreme ease. Finally, 2-naphthylamine-6 : 8-disulphonic acid does not combine with any diazo- compound. (For measurement of the rate of formation of dyestuffs, *see* Goldschmidt, Ber. 1897, 30, 670, 2075; 1899, 32, 355; 1900, 33, 893; 1902, 35, 3534; Veley, Trans. Chem. Soc. 1909, 95, 1186.)

Considering now the formation of azo- dyestuffs from tetrazotised diamines, it should be noted that diamines of the type of benzidine furnish tetrazo- compounds which can either be combined with two molecules of one component (phenol or amine) or with one molecule each of two components, and the reaction can thus be divided into two stages. This holds good even when one component only is used; thus tetrazotised benzidine combines almost at once with one molecule of naphthionic acid, forming a so-called intermediate product; but the second molecule of naphthionic acid combines with this only slowly. Here also a difference in combining power is to be noted, thus tetrazotised benzidine combines more readily than does the corresponding compound from tolidine.

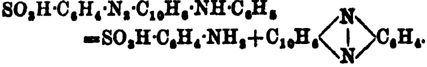
General properties.—(1) *Action of alkalis.* Hydroxyazo- dyes containing a sulphonic or carboxylic group usually form differently coloured salts, and consequently the addition of sodium hydroxide to their solutions produces a modification in the shade (compare Hewitt and Mitchell, Trans. 1907, 91, 1251). The isomeric colouring matters prepared from α- and β-naphthol show a characteristic difference in that only those derived from the former are changed by sodium hydroxide (*e.g.* benzoazurine, &c.).

(2) *Action of cold dilute acids.* Dyestuffs containing amino- or substituted amino- groups generally undergo a change when treated with dilute acid (compare Fox and Hewitt, Trans. 1908, 93, 333 ; Hewitt and Thomas, *ibid.* 1909, 95, 1292 ; Hewitt and Thole, *ibid.* 1909, 95, 1393 ; 1910, 97, 511). In the case of Congo red and methyl orange this change is so profound that these colouring matters can be used as indicators.

(3) *Action of cold concentrated sulphuric acid.* Nearly all azo- colouring matters give characteristic colour changes with this reagent, and it is often used as an aid in the detection of dyes. Mixtures of dyes, when covered with sulphuric acid, often reveal themselves by the various colours produced by the particles as they become dissolved. There are certain relationships between the colour of the solution of azo- dyes in sulphuric acid, and therefore of their absorption spectra and their chemical constitution. Thus the dyestuff from amino-azobenzenesulphonic acid and β-naphthol gives a green colour, those from the same (diazotised) amine and β-naphtholsulphonic acids, a blue, and those from aminoazobenzene and its homologues combined with β-naphtholsulphonic acids a red violet (compare Ber. 1880, 13, 1840 ; Vogel, Sitzungsber. K. Akad. Berlin, 1887, 34, 715 ; Ber. 1889, 22, 634, 2062 ; Schütze, Zeitsch. physikal. Chem. 1892, 9, 2 ; Grebe, Diss. Leipzig, 1892).

(4) *Action of hot hydrochloric acid.* Certain azo- colouring matters, such as, for example, aminoazobenzene, are decomposed when boiled with concentrated hydrochloric acid ; reduction and oxidation take place accompanied by chlorination. In the instance quoted phenylenediamine, aniline, and benzoquinone or its chloro- derivatives are produced (Wallach and Kölliker, Ber. 1884, 17, 395).

(5) *Action of hot sulphuric acid* (Witt, Ber. 1887, 20, 571). Azo- colouring matters which are derived from phenyl- or tolyl-β-naphthylamine by the action of diazo- compounds on these bases, when boiled with moderately dilute sulphuric acid, yield the bases, or their sulphonic acids, from which the diazo- compound was prepared, together with naphthazines. Thus the dyestuff obtained by combining diazotised sulphanilic acid with phenyl-β-naphthylamine, is decomposed into sulphanilic acid and phenonaphthazine :



$$SO_3H{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_6H_5$$
$$=SO_3H{\cdot}C_6H_4{\cdot}NH_2+C_{10}H_6\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle C_6H_4.$$

(6) *Action of nitric acid.* Azo- colouring matters are readily attacked by nitric acid, and the course of the reaction depends largely on the conditions of temperature and concentration. By the moderate action of nitric acid, the dyestuff may simply be nitrated, thus diphenylamine orange yields curcumeine and, by further action, azo- acid yellow, the dyestuffs in both cases, however, being accompanied by some nitrodiphenylamine produced by the fission of the azo- group. Also when flavazol

(diazotised toluidine combined with salicylic acid) is nitrated, it yields Persian yellow (*o*-nitrotolueneazosalicylic acid) (compare Ber. 1906, 40, 4207).

Methyl orange is decomposed even by cold dilute nitric acid; a methyl group is eliminated in the process, and dinitromonomethylaniline is produced. The presence of a diazo- compound can also be detected (Fox, Ber. 1908, 41, 1989).

Cold fuming nitric acid decomposes many azo- colouring matters (particularly those containing an amino- or hydroxy- group in the para- position with respect to the azo- group), with the production of the diazo- compound from which the dye is prepared and the nitro-derivative of the other component; thus, orange II yields diazotised sulphanilic acid and a nitro- derivative of β-naphthol, whilst methyl orange gives *op*-dinitrodimethylaniline, tetranitrodimethylaniline and diazotised sulphanilic acid (O. Schmidt, Ber. 1905, 38, 3201).

Certain hydroxyazo- compounds combine with two molecules of nitric acid forming unstable nitrates (Charrier and Ferreri, Gazz. chim. ital. 1913, 43, ii. 148; 1914, 44, i. 120, 165, 405).

Finally, warm nitric acid usually decomposes azo- dyestuffs, with the production of nitrophenols or bases.

(7) *Action of chlorine and bromine.* All azo-colouring matters are readily attacked by chlorine or bromine. Fission generally takes place at the azo- group with the production of halogenated phenols (compare Schmidt, J. pr. Chem. 1912, (ii.) 85, 235), but some dyestuffs are converted into substitution products (compare Ber. 1884, 17, 272).

(8) *Action of reducing agents.* Reducing agents, such as zinc-dust and water, zinc-dust and ammonia, or sodium hydroxide, zinc-dust and dilute acids, tin and hydrochloric acid, stannous chloride, a solution of sulphur in sodium sulphide (Cobenzl, Chem. Zeit. 1915, 39, 859), or sodium hyposulphite (technically known as 'hydrosulphite') (Grandmougin, Ber. 1906, 39, 2494, 3561, 3929; compare also J. pr. Chem. 1907, (ii.) 76, 124; Franzen and Stieldorf, J. pr. Chem. 1907, (ii.) 76, 467; O. Fischer, Fritzen and Eilles, J. pr. Chem. 1909, (ii.) 79, 562) attack the azo- group and convert it into two amino- groups; thus:

$$NH_2{\cdot}C_6H_4{\cdot}N:N{\cdot}C_6H_5+2H_2$$
$$=NH_2{\cdot}C_6H_4{\cdot}NH_2+C{\cdot}H_5{\cdot}NH_2.$$

The base which was used to provide the diazo-compound is thus regenerated, whilst the other component is converted into its amino-derivative.

By careful reduction with zinc-dust, dyestuffs obtained by the combination of diazotised aminoazobenzenesulphonic acid with phenols yield the aminoazosulphonic acid without the latter undergoing reduction. Further, nitro-azo- dyestuffs can be reduced to the corresponding aminoazo- dyestuffs with sodium sulphide. The reduction of azo- dyestuffs is a useful means of attacking the problem of their constitution, although the operation requires considerable care (compare Witt, Ber. 1886, 19, 1719; 1888, 21, 3468, and especially the references quoted in connection with reduction by hydrosulphite).

Azo- dyestuffs are also readily reduced by titanous chloride, and a process for their estimation by titration with this reagent has been worked out by Knecht (J. Soc. Dyers, 1903, 19, 169; Ber. 1903, 36, 166, 1549; 1907, 40, 3819). A detailed account of the method of carrying out this and other methods of reduction[1] will be found in Knecht and Hibbert's New Reduction Methods in Volumetric Analysis (Longmans).

(9) *Action of sodium bisulphite.* When boiled with aqueous-alcoholic sodium bisulphite solution, hydroxyazo- colouring matters give sulphurous esters, the hydroxyl group being converted into $O{\cdot}SO_2Na$ (Voroshcov, J. Russ. Phys. Chem. Soc. 1911, 43, 771; 1915, 47, 1669; published in French in Ann. Chim. 1916, [ix.] 6, 381; 1917, 7, 50). In aqueous solution fission takes place (Lepetit and Levi, Gazz. chim. ital. 1911, 41, i. 675).

Identification of azo- colouring matters on the fibre. This is carried out by observing the action on the dyed fabric of various reagents, for which various tables have been constructed (compare Cain and Thorpe, The Synthetic Dyestuffs, 4th ed. 1918; Lunge, Chemisch-technische Untersuchungensmethoden, Eng. trans., edited by Keane, 1911; Green, The Analysis of Dyestuffs).

Direct formation of azo- colours in the fibre.—The production of an insoluble azo- dyestuff in the fibre was first achieved by T. and R. Holliday (E. P. 2757 of 1880), who impregnated the fibre with α- or β-naphthol, passed it then through a diazo- solution, and finally developed the colour by treatment with alkali. An improvement on this process was introduced by the Farbwerke vormals Meister, Lucius und Brüning, in 1889, which consisted in 'padding' the fibre (generally cotton) with the sodium salt of a phenol (usually β-naphthol), and passing the cloth through a diazo- solution, the free mineral acid of which has been neutralised by adding sodium acetate. This process is very largely used at the present day, and is applied to the greatest extent to the production of the so-called 'para-red' (the azo- colour obtained by combining diazotised *p*-nitroaniline with β-naphthol). The colouring matters produced in this way will now be described.

Paranitraniline Red. The colouring matter was first prepared in substance by Meldola (Chem. Soc. Trans. 1885, 47, 657) by combining diazotised *p*-nitroaniline with β-naphthol in alkaline solution. As stated above, it is now almost entirely produced on the fibre. The goods are soaked in a bath containing sodium β-naphthoxide and Turkey-red oil, or thickening materials, squeezed out and dried at 65°–80°. They are then passed through the diazo- solution, washed and soaped. In order to avoid preparing the diazo- solution in the dye-house, various preparations may be used. Thus, **Paranitraniline extra N** paste is a mixture of *p*-nitroaniline with the calculated amount of sodium nitrite, and needs only to be stirred slowly into the necessary quantity of hydrochloric or sulphuric acid, ice, and water, to produce the diazo-solution. A similar product is **Benzonitrol**

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[1] For the estimation with sodium hyposulphite, *see* Grandmougin and Havas, Chem. Zeit. 1912, 36, 1167.

paste. Other preparations contain the diazo- compound in a suitable form for keeping. Thus, **Nitrosamine Red** is the sodium salt of *p*-nitro*anti*diazobenzene (which is very stable) and furnishes the true diazo- solution when mixed with dilute acid. **Azophor Red, Azogen Red** and **Nitrazol C,** are mixtures of the diazo-sulphate with sodium sulphate (whereby sodium hydrogen sulphate is produced); they are dissolved in water, the solution filtered, if necessary, and neutralised before use with sodium acetate or hydroxide. **Paranil** is a stable compound of diazotised *p*-nitroaniline and naphthalene-β-sulphonic acid. Paranitraniline red is used as a substitute for the red Congo dyestuffs and for Turkey red. It is extracted from the fibre when treated with organic solvents, and when the fibre is heated to 180°–200° the dyestuff partly sublimes. (For the formation of paranitraniline red, *see* Pomeranz, Zeitsch. Farben. Ind. 1906, 5, 184; Erban and Mebus, Chem. Zeit. 1907, 31, 663, 678, 687; Lichtenstein, Zeitsch. Elektrochem. 1908, 14, 586; Prud'homme and Colin, Rev. Gen. Mat. Col. 1909, 13, 1, 66; Bull. Soc. chim. 1909, (iv.) 5, 779; Bucherer, and Wolff, Zeitsch. angew. Chem. 1909, 22, 731; Justin-Mueller, Bull. Soc. chim. 1910, (iv.) 7, 60.) When in the form of a lake it is known as **Pigment Red G** (M.[1]); **Autol Red BGL** (B.); **Sitara Red** (T. M.).

Metanitraniline Orange and **Nitro-*o*-toluidine Orange**. Prepared as above from diazotised *m*-nitroaniline or *p*-nitro-*o*-toluidine and β-naphthol. The former gives yellowish and the latter reddish shades of orange. Their use is not very extensive, as they are not fast to rubbing, and the colours sublime on keeping. An orange free from these disadvantages can, however, be obtained by using *m*-nitro-*p*-phenetidine.

Nitro-*o*-toluidine orange, in the form of a lake, is sold as **Pigment Orange R** (M.); **Fast Orange** (By.).

Nitrophenetidine Rose or **Blue-red**. Here *o*-nitro-*p*-phenetidine is used as the diazotised base.

Azophor Rose A (M.) is the stabilised diazo-compound of *o*-anisidine. The compound of diazotised *o*-anisidine and β-naphthol is used as a lake under the names **Pigment Purple A** (M.); **Sudan R** (A.).

Naphthol Rose is the stabilised diazo- compound of *p*-nitro-*o*-anisidine.

Literature.—E. P. 25756 of 1897; D. R. P. 98637; F. P. 271908.

Chloranisidine Scarlet (M.) is produced on the fibre by the aid of diazotised *p*-chloro-*o*-anisidine.

Naphthylamine Bordeaux. Prepared on the fibre from diazotised α-naphthylamine[2] and β-naphthol. The dyestuff is used also as a pigment colour under the names **Carminaph Garnet** (D. H.), **Cerotine Scarlet 2 R** (C. J.), &c.

Azo Turkey Red is produced by treating cloth padded with β-naphthol with diazotised β-naphthylamine. It is a bright scarlet, which, however, is not very fast.

Fast Azo Garnet. Prepared from diazotised *o*-aminoazotoluene and β-naphthol. It is also manufactured in substance and is used for colouring oils and varnishes under the names **Oil Scarlet** (M) (K) (W), **Red B, Oil soluble, extra conc.** (Remy), **Cerotine Ponceau 3 B** (C. J.), and **Fat Ponceau R** (K).

Benzidine and **Tolidine Puce.** Obtained from tetrazotised benzidine or tolidine and β-naphthol. Dark garnet to brown shades are produced which, however, are not fast to light. Rather yellower shades result by using tetrazotised diaminocarbazole instead of these diamines; when treated with copper salts the tints are very fast to light.

Dianisidine Blue. Tetrazotised dianisidine is combined on the fibre with β-naphthol in presence of copper salts. The tetrazo-compound is also put on the market as **Azophor Blue D,** a mixture of the tetrazo- compound and aluminium sulphate which has been dried in a vacuum at 45°. The colour is very fast to light, soap, and rubbing. **Azophor Black S** is a stabilised mixture of the tetrazo- compound of dianisidine with other diazo- compounds (from benzidine, *p*-nitroaniline, and especially *m*-nitroaniline, *cf.* D. R. P. 83963).

The production of black insoluble colours in the fibre was first effected by the Farbwerke vorm. Meister, Lucius und Brüning. The cloth is padded with β-naphthol and tragacanth, and treated with a mixture of the tetrazo-compounds of dianisidine and certain other bases. The mixture of bases sold for this purpose is known as **Azo Black Base O,** and the diazo- compounds are put on the market under the name of **Azophor Black S.** Cassella & Co. have introduced a black obtained by padding the cloth with 1 : 6- or 1 : 7-aminonaphthol, and then passing it through diazotised *p*-nitroaniline so as to form the disazo- colouring matter. The aminonaphthol is put on the market as **Amidonaphthol BD** and **3 B,** and both brands are mixtures of the two aminonaphthols mentioned. Full black colours are obtained which are fast to soap and chlorine, but they are not very easily applied in printing. A black, also introduced by the same firm, is produced from **Azotol C,** which is an asymmetric dialkylated di-*p*-diaminoazobenzene (it is identical with Kinzlberger's **Ice Black**). The base is diazotised and combined with β-naphthol on the fibre in the usual way. The latter firm also has introduced the use of the diazo- compound of aminochrysoïdine, and of the tetrazo- compound of *pp*-diaminodiphenylamine for the production of black colours. Other tetrazo-compounds recommended are these of amino-benzene-azo-α-naphthylamine (By.) and diamino-dimethylcarbazole (M.).

Nigrophor BASF (B.). Diazotised 2 : 5-dichloroaniline is combined with 1-amino-8-naphthol-5-sulphonic acid in acid solution, the monoazo- dye is dissolved in sodium hydroxide solution, mixed with *p*-nitrophenylnitrosamine and cloth padded with the solution. After being dried and exposed to the air a greenish-black is produced on the fibre. α-Naphthylamine may also be used instead of *p*-nitroaniline.

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[1] See p. 458 for the full names of firms of which these letters are a contraction.

[2] Finely ground α-naphthylamine sulphate is sold as α-Naphthylamine salt S, and a stable compound of diazotised α-naphthylamine with α-naphthalene-disulphonic acid as Naphthol garnet 50 p.c. paste.

Literature.—E. P. 1002 of 1895; D. R. P. 116676; F. P. 24424, 245211.

Another process of producing azo- colouring matters on the fibre is by the use of primuline (*q.v.*). When cotton dyed with this dyestuff is treated with a solution containing hydrochloric acid and sodium nitrite, the dyestuff is diazotised. The cloth is now passed through a bath containing the 'developer,' consisting of a solution of an amine or a phenol. β-Naphthol is mostly used in giving **Ingrain-** or **Primuline Red**. An orange colour is obtained with resorcinol (**Ingrain Orange**), and a brown with *m*-phenylenediamine (**Ingrain Brown**). Many direct-dyeing cotton colours which contain a diazotisable amino- group (for example, diamine black BH) acquire a faster, deeper, and modified shade when similarly diazotised on the fibre and developed with β-naphthol or *m*-phenylenediamine.

In the succeeding portion of this article it is proposed to give an account of the most important azo- colours which are at present in commerce. Each colour will be treated of under its commercial name; its chemical formula given, and the mode of preparation and general properties briefly described.

Unless otherwise stated, it may be assumed that colouring matters containing a sulphonic or carboxylic group are placed on the market in the form of their sodium salts.

The following abbreviations are used for the names of firms [1]:—

(A.) = Aktiengesellschaft für Anilinfabrikation, Berlin.
(B.) = Badische Anilin- und Soda-Fabrik, Ludwigshafen a/Rhein.
(B.K.) = Leipziger Anilinfabrik Beyer & Kegel.
(By.) = Farbenfabriken vorm. Fr. Bayer & Co., Elberfeld.
(C.) = Leopold Cassella & Co., Frankfurt a/Main.
(C. J.) = Carl Jäger, G. m. b. H., Düsseldorf-Derendorf.
(Cl. Co.) = The Clayton Aniline Co., Ltd., Clayton, Manchester.
(Claus & Co.) = Claus & Co., Clayton, Manchester (since 1917 amalgamated with Levinstein, Ltd.).
(D.) = Wülfing, Dahl & Co., Barmen.
(D. H.) = Dye Works, formerly L. Durand, Huguenin, & Co., Basle.
(F.) = A. Fischesser & Co., Lutterbach.
(G.) = Aniline Colour- and Extract-Works, formerly John R. Geigy, Basle.
(H.) = Read Holliday and Sons, Ltd., Huddersfield (now British Dyestuffs Corporation, Ltd., Huddersfield branch).
(I.) = Société pour l'Industrie Chimique, (formerly Bindschedler und Busch), Basle.
(K.) = Kalle & Co., Biebrich a/Rhein.
(K. S.) = Sandoz & Co. (formerly Kern and Sandoz), Basle.
(L.) = Farbwerk Mülheim (formerly A. Leonhardt & Co.), Mülheim, near Frankfurt.
(Lev.) = Levinstein, Ltd., Blackley, Manchester (now British Dyestuffs Corporation, Ltd., Blackley branch).
(M.) = Farbwerke vorm. Meister, Lucius, und Brüning, Höchst a/Main.
(N. I.) = Farbwerk Griesheim, Nötzel, Istel & Co., Griesheim a/Main.
(O.) = Chemische Fabrik Griesheim-Elektron, Werk Oehler (formerly K. Oehler), Griesheim.
(P.) = Société Anonyme des Matières Colorantes & Produits Chimiques de St. Denis, Paris.
(Sch.) = The Schöllkopf Aniline and Chemical Company, Buffalo, U.S.A. (since 1917 is included in The National Aniline and Chemical Co., Inc., New York).
(T. M.) = Chemische Fabriken vorm. Weiler ter Meer, Uerdingen a/Rhein.
(W.) = Williams Bros. & Co., Hounslow, Middlesex.

Also E. P. = English Patent; D. R. P. = German Patent; F. P. = French Patent; A. P. = American Patent.

I. Basic Azo- Compounds.

Aniline Yellow; Aminoazobenzene

$$C_6H_5{\cdot}\underset{[1]}{N_2}{\cdot}C_6H_4{\cdot}\underset{[4]}{NH_2}$$

This compound, discovered by Mène in 1861 (*l.c.*), and introduced into commerce by Simpson, Maule, and Nicholson in 1863, is interesting as being the first azo- colour made on a manufacturing scale. It was formerly prepared by passing nitrous acid gas into an alcoholic solution of aniline. As a colouring matter it is now of no importance, but is largely used as the starting-point in the manufacture of other azo- colours and of indulines. In practice this compound cannot be prepared directly by the action of one molecule of nitrous acid on two molecules of aniline, since diazoaminobenzene is always the first product of this reaction:

$$2C_6H_5{\cdot}NH_2,HCl+NaNO_2$$
$$=C_6H_5{\cdot}N_2{\cdot}NH{\cdot}C_6H_5+NaCl+HCl+2H_2O.$$

The diazo- compound is slowly converted into the isomeric aniline yellow on being kept for some time in contact with aniline and an aniline salt:

$$C_6H_5{\cdot}N_2{\cdot}NH{\cdot}C_6H_5=C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}NH_2.$$

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[1] Since the last edition of this 'Dictionary' was published a great revival of the Dye Industry has taken place in England, France, Italy, America, Sweden, and Japan. The principal new companies which have been formed are British Dyes, Ltd. (later incorporated with Levinstein Ltd., under the name of British Dyestuffs Corporation, Ltd.), Compagnie Nationale des Matieres Colorantes et Produits Chimiques (France), Italian National Dyestuff Co. (Italy), The National Aniline and Chemical Co., Inc. (America), The A.B. Kemisk Industrie (Sweden), and The Japan Dyestuff Co. (Japan). Other new firms manufacturing azo- colouring matters are indicated under the particular dyes.

The manufacture is carried out as follows: 100 kilos. of aniline are mixed with 36 kilos. of concentrated hydrochloric acid, the mixture cooled (from outside) to about 18°, and a solution of 15·5 kilos. of sodium nitrite in 18 kilos. of water and 18 kilos. of saturated sodium chloride solution added at first fairly rapidly, so that the temperature rises to 25°, and then more slowly, the temperature being kept below 28° by outside cooling. This operation takes about 7–8 hours. After 24 hours the change of diazoaminobenzene into aminoazobenzene is complete. The salt solution is now drawn off, the residue stirred with 96 kilos. of hydrochloric acid and 64 kilos. of water, and the aminoazobenzene hydrochloride is filtered off, washed with 2 p.c. hydrochloric acid, centrifuged and dried at 60°. The yield is 41 kilos. of dry aminoazobenzene hydrochloride. The old aniline yellow was the oxalate of the base. The free base crystallises in yellow rhombic prisms. M.p. 127·4°; b.p. above 300°. The hydrochloride crystallises in steel-blue needles. Base slightly soluble in hot water, readily soluble in alcohol. Yellow solution coloured red by hydrochloric acid.

Literature.—Mène, 1861 (*see* above); Dale and Caro, E. P. 3307 of 1863; Martius und Griess, Zeitsch. f. Chem. 1866, 2, 132; Kekulé, *ibid.* 2, 689; Witt and Thomas, Chem. Soc. Trans. 1883, 43, 112; Friswell and Green, *ibid.* 1885, 47, 917; and 1886, 49, 746; Stadel and Bauer, Ber. 1886, 19, 1953; Paul, Zeitsch. angew. Chem. 1896, 9, 689; Jansen, Zeitsch. Farb. Ind. 1913, 12, 197.

Spirit Yellow R (K.); **Yellow Fat Colour**; *o*-Aminoazotoluene

$$CH_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(CH_3){\cdot}NH_2$$

Prepared similarly to aniline yellow, from *o*-toluidine.

Literature.—Ber. 1877, 10, 662.

Butter Yellow; **Oil Yellow** (W.); Dimethylaminoazobenzene $C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N(CH_3)_2$. Prepared by the action of diazobenzene chloride on dimethylaniline. Substance forms yellow leaflets of m.p. 115°; soluble in dilute hydrochloric acid with a red colour; precipitated by alkali. Soluble in sulphuric acid[1] with a yellow colour, becoming red on dilution.

Literature.—Griess, Ber. 1877, 10, 528.

Chrysoïdine (most firms); **Chrysoïdine Y** (H). (W.) (Marden, Orth, and Hastings Corp. New York) (Sch.); **Chrysoïdine JEE** (C. J.) (P.); **Chrysoïdine Crystals**[2]; **Chrysoïdine Small Crystals** (T. M.)

Diaminoazobenzene $C_6H_5{\cdot}\underset{[1]}{N_2}{\cdot}C_6H_3\underset{[2:4]}{(NH_2)_2}$.

This colouring matter is prepared by mixing a solution of diazobenzene chloride with a solution of *m*-phenylenediamine. In practice a known weight of aniline is dissolved in dilute hydrochloric acid and diazotised, the solution being diluted so as to contain about 2–3 p.c. of diazo- salt. This and a dilute solution of phenylenediamine hydrochloride are run simultaneously into a sodium chloride solution, and the colouring matter is filtered off through a filter press. The press cake is then dissolved in hot dilute hydrochloric acid, the hot solution filtered, and hydrochloric acid added to the filtrate. The chrysoïdine separates in small needles, which are filtered off, centrifuged, and dried at 50°. The free base forms yellow needles; m.p. 117·5°. Slightly soluble in water, readily in alcohol; solutions orange. The commercial product is the hydrochloride $C_{12}H_{12}N_4,HCl$, which forms beautiful blackish-green prisms with a metallic lustre. The strong solution of the salt solidifies on rapid cooling to a red jelly. Dissolves in sulphuric acid with a brownish-yellow colour.

Literature.—Hofmann, Ber. 1877, 10, 213; Witt, *ibid.* 350 and 654; Griess, *ibid.* 389.

Chrysoïdine R (H.) (W.) (G.) (I.) (Sch.); **Chrysoïdine REE** (P.); **Cerotine Orange** (C. J.); **Gold Orange for Cotton** (T. M.) (D. H.); Benzeneazo-*m*-tolylenediamine

$$C_6H_5{\cdot}N_2{\cdot}C_6H_2(CH_3)(NH_2)_2$$

Prepared from aniline and *m*-tolylenediamine as in the preceding case. The free base melts at 165°–166°. The commercial product is the hydrochloride, which forms yellowish-brown lumps. Dissolves in sulphuric acid with a greenish-yellow colour.

Chrysoïdine R (D. H.) (C.); Tolueneazo-*m*-tolylenediamine $CH_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_2(CH_3)(NH_2)_2$. Prepared as above from *o*-toluidine and *m*-tolylenediamine. The commercial product is the hydrochloride. It is a crystalline violet powder which gives a brown colour in sulphuric acid.

Meta Chrome Brown B (A.) (Brotherton & Co.); Dinitrophenolazo-*m*-tolylenediamine

$$OH{\cdot}C_6H_2(NO_2)_2{\cdot}N_2{\cdot}C_6H_2(CH_3)(NH_2)_2$$

Prepared from picramic acid and *m*-tolylenediamine. It is a brown paste giving a dark orange-red solution in hot water. It yields a red solution with sulphuric acid.

Literature.—E. P. 13213 of 1899; 10294 of 1910; D. R. P. 112819, 118013; A. P. 657064, 657065.

Chrome Brown P (P.); Dinitrophenolazo-*m*-aminophenol $OH{\cdot}C_6H_2(NO_2)_2{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}NH_2$. Prepared from picramic acid and *m*-aminophenol. Introduced in 1903.

Literature.—D. R. P. 169579; F. P. 336559.

Meta Chrome Bordeaux R, B (A.). Prepared from diazotised picramic acid and a *m*-aminoarylsulphamide. The **R** brand gives an orange-brown solution in hot water, and a reddish-violet solution in sulphuric acid, which yields a brown precipitate on dilution.

Literature.—E. P. 4028 of 1902; D. R. P. 135016; A. P. 704825, 704826.

Diazine Green S (K.); **Janus Green B** (M.); **Union Green B** (M.). Prepared from diazotised safranine and dimethylaniline. The commercial product is a brown or dark-green powder giving an olive-green solution with sulphuric acid. **Janus Green G** is a dyestuff of analogous constitution.

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[1] In these colour reactions 'sulphuric acid' means the ordinary concentrated acid of 95 96 per cent.

[2] Chrysoïdine Crystals also contain the homologues from *o*- and *p*-toluidine.

Literature.—E. P. 7337 of 1897; F. P. 265438; D. R. P. 95668.

II. Acid Azo- Compounds.

A. Sulphonic Acids of Aminoazo- Compounds.

Acid Yellow (A.); **Fast Yellow** (B.) (By.); **Fast Yellow G**; **New Yellow L** (K.); **Yellow SS** (P.); **Fast Yellow extra** (By.). This colouring matter is a mixture of the sodium salts of mono- and di- sulphonic acids of aminoazobenzene

$$HSO_3\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NH_2 \text{ and}$$
$$HSO_3\cdot C_6H_4\cdot N_2\cdot C_6H_3(HSO_3)\cdot NH_2$$

Prepared by the action of fuming sulphuric acid on aniline yellow (3–5 parts acid to one of aminoazobenzene). Solution not precipitated by alkali; colour dissolves in sulphuric acid with a brownish-yellow colour becoming redder on dilution. Solution gives a precipitate with barium chloride, but not with calcium chloride. The corresponding colouring matter from aminoazotoluene is somewhat more orange in shade, and is known as **Fast Yellow Y** (B.); **Fast Yellow R** (K.).

Literature.—Grässler, E. P. 43 of 1879; A. P. 253598; D. R. P. 4186, 7094; Chem. Ind. 1879, 2, 48, 346; Griess, Ber. 1882, 15, 2187; Eger, Ber. 1889, 22, 847.

Methyl Orange (Consolidated Colour and Chemical Co., New Jersey); **Helianthin** (B.); **Orange III.** (P.) (T. M.) (D. H.) (W.); **Gold Orange** (A.); *p*-Sulphobenzeneazodimethylaniline $\underset{[4]}{HSO_3}\cdot C_6H_4\cdot \underset{[1]}{N_2}\cdot C_6H_4\cdot \underset{[4]}{N(CH_3)_2}$. Prepared by the action of diazotised sulphanilic acid [1] on dimethylaniline. Solution of colouring matter orange, and not precipitated by alkali; dilute acids produce a crystalline precipitate, the crystals having a violet reflection (the free sulphonic acid). The substance dissolves in sulphuric acid with a yellow colour becoming red on dilution.

Literature.—Griess, Ber. 1877, 10, 528.

Orange IV. (most firms); **Tropæoline OO** (C.); **Acid Yellow D** (A.); **Orange N** (B.) (I.); **New Yellow** (By.); *p*-Sulphobenzeneazodiphenylamine $\underset{[4]}{HSO_3}\cdot C_6H_4\cdot \underset{[1]}{N_2}\cdot C_6H_4\cdot \underbrace{NH\cdot C_6H_5}_{[4]}$. Produced by the action of diazotised sulphanilic acid on diphenylamine dissolved in alcohol or crude carbolic acid. The product is thrown on an open filter, the paste dissolved in concentrated aqueous potassium carbonate and precipitated by adding sodium hydroxide. The colouring matter is not very readily soluble in water; the solution is yellow, and when strong deposits crystals on cooling. Substance dissolves in sulphuric acid with a violet colour, becoming redder and giving a greyish precipitate of the free sulphonic acid on dilution. The aqueous solution of the substance is coloured red by dilute acids.

When nitrated this colour furnishes a mono-nitro- derivative together with a mixture of mono-, di-, and tri- nitrodiphenylamine; moderate nitration yields a yellow colouring matter which is found in commerce under the names of **Citronine** (D. H.) (I.) (L.) (K. S.) (O.); **Curcumeine** (A.); **Azoflavine 3 R** ex. conc (T. M.); **Citronine NE** (P.); **Indian Yellow R** (By.) (C.) (H.). More energetic nitration of Orange IV. furnishes **Azo Acid Yellow** (A.); **Azo Yellow** (K.) (K. S.) (M.); **Azo Yellow 3 G**, ex. conc. (T. M.); **Citronine 2 AEJ** (P.); **Azoflavine S new** (B.); **Indian Yellow G** (By.). Both dyestuffs are ochre-yellow powders and give with sulphuric acid reddish-violet and magenta-red solutions respectively.

Metanil Yellow (most firms); **Orange MN** (I.); **Tropæoline G** (C.); **Yellow M** (P.); **Metanil Yellow GR extra** (T. M.); *m*-Sulphobenzeneazodiphenylamine $\underset{[3]}{HSO_3}\cdot C_6H_4\cdot \underset{[1]}{N_2}\cdot C_6H_4\cdot \underbrace{NH\cdot C_6H_5}_{[4]}$. Prepared in the same manner as the preceding from *m*-diazobenzenesulphonic acid [1] and diphenylamine. Aqueous solution orange, giving no precipitate with alkalis, becoming red and precipitating with dilute acids. Dissolves in sulphuric acid with a dull violet colour, becoming magenta-red on dilution.

Metanil Yellow S; **Acid Yellow 2 G** (O.); is produced by sulphonating the preceding colouring matter.

Literature.—E. P. 1226 of 1879; 4966 of 1880; Paul, Zeitsch. angew. Chem. 1896, 9, 686.

Metanil Yellow Brominated (P.). Prepared by the action of bromine on metanil yellow; has similar reaction.

Literature.—E. P. 5696 of 1882; D. R. P. 26642; F. P. 140114.

Jaune Solide N (P.); Sulphotolueneazodiphenylamine $HSO_3\cdot C_7H_6\cdot \underset{[1]}{N_2}\cdot C_6H_4\cdot \underbrace{NH\cdot C_6H_5}_{[4]}$. Prepared from diazotised *p*-toluidine-*o*-sulphonic acid and diphenylamine; in its general properties it resembles the two preceding dyes.

Literature.—Roussin and Poirrier, E. P. 4491 of 1878.

Archil Substitute V; *p*-Nitrobenzeneazo-*a*-naphthylamine-4-sulphonic acid

$$NO_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_5(NH_2)\cdot HSO_3$$

Prepared by the action of diazotised *p*-nitroaniline on naphthionic acid [2] in weakly acid solution. Solution precipitated by acids and alkalis. Sulphuric acid gives a magenta-red solution, becoming brownish and precipitating on dilution.

Literature.—Roussin and Poirrier, E. P. 4490 of 1878; D. R. P. 6715; F. P. 127221; Chem. Ind. 1879, 2, 292.

Archil Substitute 3 VN (P.); *p*-Nitrobenzeneazo-*a*-naphthylaminesulphonic acid

$$NO_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_5(NH_2)\cdot SO_3H$$

Prepared by the action of diazotised *p*-nitroaniline on *a*-naphthylamine-5-sulphonic acid.

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[1] For detailed information on the manufacture of sulphanilic acid and its homologues *see* Mühlhäuser, Dingl. poly. J. 1887, 264, 181 and 238; Paul, Zeitsch. angew. Chem. 1896, 9, 686.

[1] *m*-Aminobenzenesulphonic acid is prepared by sulphonating nitrobenzene and reducing the *m*-nitrobenzenesulphonic acid thus formed.

[2] Naphthionic acid is manufactured on a large scale by heating naphthylamine acid sulphate, mixed with a little oxalic acid, to about 180°.

Forms a brown powder giving a red solution in water or sulphuric acid.

Literature.—E. P. 12692 of 1887; D. R. P. 45787; F. P. 185908.

Azo Cardinal G (A.); *p*-Nitrobenzeneazobenzylethylanilinesulphonic acid

$$NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot N(C_2H_5)\cdot CH_2\cdot C_6H_4\cdot SO_3H$$

Prepared by the action of diazotised *p*-nitroaniline on benzylethylanilinesulphonic acid. A brick-red powder giving a reddish-yellow solution in water and a yellow solution in sulphuric acid, becoming red on dilution

Literature.—D. R. P. appl. A 3551.

Palatine Chrome Brown W (B.); **Acid Alizarine Brown B** (M.); **Anthracyl Chrome Brown D** (D.); *p*-Sulpho-*o*-hydroxybenzeneazo-*m*-phenylenediamine

$$SO_3H\cdot C_6H_3(OH)\cdot N_2\cdot C_6H_3(NH_2)_2$$

Prepared from diazotised *o*-aminophenol-*p*-sulphonic acid and *m*-phenylenediamine. A black-brown powder dissolving in hot water with an orange-brown colour, and in sulphuric acid to give a dark orange-brown solution.

Literature.—A. P. 628814; D. R. P. 78409; F. P. 284741.

Omega Chrome Black PV, PB (K. S.); **Omega Chrome Blue B, R** (K. S.) are chrome colours prepared from *o*-diazophenols and aryl-1 : 8-naphthylaminesulphonic acids.

Literature.—E. P. 22738 of 1905; D. R. P. 175625; F. P. 359222; A. P. 841371.

Acid Anthracene Brown R (By.) is prepared from diazotised picramic acid and substituted phenylenediaminesulphonic acids. The aqueous solution is reddish-brown, and that in sulphuric acid is reddish-violet, becoming yellowish-brown on dilution.

Anthracyl Chrome Green (D.); Dinitrophenolazo-*a*-naphthylamine-4-sulphonic acid

$$OH\cdot C_6H_2(NO_2)_2\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2$$

Prepared by the action of diazotised picramic acid on naphthionic acid. Solution in water is reddish-brown, and in sulphuric acid bluish fiery red.

Literature.—D. R. P. 142153.

Alkali Brown (D.); **Benzo Brown 5 R** (By.); **Alkali Brown R** (L. P.); Primulineazo-*m*-phenylenediamine $P^1\cdot N_2\cdot C_6H_3(NH_2)_2$. Prepared from diazotised primuline or dehydrothio-*p*-toluidinesulphonic acid and *m*-phenylenediamine. Solution brownish-red, precipitated by acids or alkalis. Gives a bluish-violet solution with sulphuric acid.

Pyramine Yellow R (B.) Diazotised primuline is combined with nitro-*m*-phenylenediamine. Aqueous solution is reddish-yellow, and solution in sulphuric acid is brownish-yellow.

Literature.—E. P. 8564 of 1894; D. R. P. 80973; F. P. 238340.

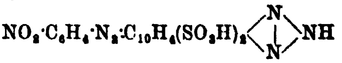
Cotton Orange G (B.); Diazotised primuline is combined with *m*-phenylenediaminedisulphonic acid. It gives an orange-yellow solution in water, and a brownish-orange in sulphuric acid.

Literature.—E. P. 14678 of 1893; D. R. P. 73369; F. P. 231694; A. P. 524262.

Apollo Red (G.); **Archil Substitute extra** (C.); *p*-Nitrobenzeneazo-a-naphthylaminedisulphonic acid, $NO_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_4(NH_2)(SO_3H)_2$. Prepared from diazotised *p*-nitroaniline and *a*-naphthylamine-4 : 6- or 4 : 7-disulphonic acid. Gives a brownish-red solution in water and a magenta-red in sulphuric acid.

Literature.—E. P. 9468 of 1887 A. P. 376392; F. P. 184638.

Brilliant Archil C (C.); Azimide of *p*-nitrobenzeneazo-1 : 8-naphthylenediaminedisulphonic acid



$$NO_2\cdot C_6H_4\cdot N_2{:}C_{10}H_4(SO_3H)_2\langle N_2H \rangle NH$$

Prepared by the action of nitrous acid on the product from diazotised *p*-nitroaniline and 1 : 8-naphthylenediamine-3 : 6-disulphonic acid. A brownish-red powder dissolving in water with a red, and in sulphonic acid with a blue, solution.

Literature.—E. P. 24714 of 1893; D. R. P. 77425; F. P. 234837.

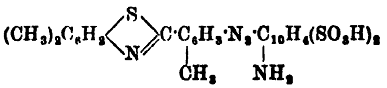
Wool Violet S (B.); Dinitrobenzeneazodiethylmetanilic acid

$$(NO_2)_2C_6H_3\cdot N_2\cdot C_6H_3(SO_3H)\cdot N(C_2H_5)_2$$

Prepared from diazotised 2 : 4-dinitroaniline and diethylmetanilic acid. A black powder giving a reddish-violet solution in water and a scarlet-red in sulphuric acid.

Literature.—E. P. 6197 of 1894; D. R. P. 86071; F. P. 239096; A. P. 525656.

Salmon Red (A.); Methylbenzenylaminothioxylenolazo-*β*-naphthylamine-3 : 6-disulphonic acid



$$(CH_3)_2C_6H_2\langle {}^{S}_{N} \rangle C\cdot C_6H_3(CH_3)\cdot N_2\cdot C_{10}H_4(SO_3H)_2(NH_2)$$

Prepared from diazotised dehydrothio-*m*-xylidine and *β*-naphthylamine-3 : 6-disulphonic acid R. Aqueous solution is orange-red. Gives violet solution in sulphuric acid.

Literature.—Paul, Zeitsch. angew. Chem. 1896, 9, 680.

Brilliant Yellow S (B.) (T. M.) (B K.); **Yellow WR** (I.); **Curcumine** (G.); *p*-Sulphobenzeneazodiphenylaminesulphonic acid. Prepared by sulphonating orange IV. Solution in water is yellow and in sulphuric acid bluish-red.

Literature.—D. R. P. 21903.

Lanacyl Violet B (C.); Disulphohydroxynaphthaleneazoethyl-a-naphthylamine

$$(HSO_3)_2C_{10}H_4(OH)\cdot N_2\cdot C_{10}H_6\cdot NH\cdot C_2H_5$$

Prepared from diazotised 1 : 8-aminonaphthol-3 : 6-disulphonic acid and ethyl-*a*-naphthylamine. Solution in water is reddish violet, and in sulphuric acid is greenish-blue.

Literature.—E. P. 12556 of 1896; D. R. P. 94288; F. P. 257136.

Tolyl Blue SR (M.); **Sulphone Acid Blue R** (By.). Prepared, as the preceding, from diazotised H-acid and 1-phenylnaphthylamine-8-sulphonic acid. Solution in water is reddish-violet, and in sulphuric acid dirty blue. The corresponding colouring matter with the tolyl-substituted acid is **Tolyl Blue SB** (M.); **Sulphone**

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[1] P = the residue of primuline.

Acid Blue B (By.); **Brilliant Cloth Blue III. F** (K.); it dissolves in water to a reddish-blue, and in sulphuric acid to a dirty violet solution.

Literature.—E. P. 24830 of 1898; D. R. P. 75571, 108546.

B. Carboxylic Acids of Aminoazo- Compounds.

Yellow fast-to-soap (P.); *m*-Carboxybenzeneazodiphenylamine

$$CO_2H{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_5$$

Prepared by the action of *m*-diazobenzoic acid on diphenylamine. Used in wool-dyeing and especially calico-printing; the shades are very fast to soap. A brown paste, sparingly soluble in water. Solution becomes reddish-violet with acids. Dissolves with a violet colour in sulphuric acid, becoming red on dilution.

Literature.—E. P. 4621 of 1883; D. R. P. 29961; F. P. 157755; A. P. 297852.

C. Hydroxyazo- Compounds.

Sudan Brown (A.) (Sch.); **Brown G** (C. J.); **Pyronal Brown** (D.); **Oil Brown** (Farbwerk Ammersfoort) (Wiescher & Co.); α-Naphthaleneazo-α-naphthol $C_{10}H_7{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$. Prepared by the action of diazotised α-naphthylamine on α-naphthol in alkaline solution.

Literature.—E. P. 786 of 1878; D. R. P. 5411; F. P. 123148; A. P. 204799; Frankland, Trans. Chem. Soc. 1880, 37, 752.

Sudan G (A.) (W.); **Carminaph J** (D. H.); **Cerasine Orange G** (C.); **Cerotine Yellow R** (C. J.); **Chrysoïn insoluble** (P.); **Pyronal Yellow** (D.); **Oil Orange** (I.); Benzeneazoresorcinol $C_6H_5{\cdot}N_2{\cdot}C_6H_3(OH)_2$. Prepared by the action of diazobenzene chloride on resorcinol in alkaline solution. Solution of colouring matter in alkali hydroxide is orange-yellow, giving a brown precipitate with acids. Dissolves in sulphuric acid with a yellowish-brown colour.

Literature.—Baeyer and Jager, Ber. 1875, 8, 151; Typke, *ibid.* 1877, 10, 1576; Wallach, *ibid.* 1881, 14, 24; Wallach and Fischer, *ibid.* 1882, 15, 2814; Meyer and Kreis, *ibid.* 1883, 16, 1329; Liebermann and Kostanecki, *ibid.* 1884, 17, 880; Heumann and Oeconomides, *ibid.* 1887, 20, 904; Will and Pukall, *ibid.* 1120; Pukall, *ibid.* 1147; Fischer and Wimmer, *ibid.* 1578; Will, *ibid.* 1888, 21, 604; Kostanecki, *ibid.* 3119.

Sudan I (A.) (K.) (W.); **Carminaph** (D. H.); **Cerotine Orange G** (C. J.); **Oil Orange** (O.) (Farbwerk Ammersfoort) (Wiescher & Co.); **Motl Orange R** (T. M.); **Pyronal Orange** (D.); **Spirit Orange** (L.); **Scarlet B** (B. K.); **Oil Yellow** (Sch.); **Insoluble Aniline Orange** (P.); Benzeneazo-β-naphthol $C_6H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$. Prepared from diazobenzene chloride and β-naphthol. A brick-red powder insoluble in water. Used for colouring oils, &c.

Literature.—Liebermann, Ber. 1883, 16, 2860; Denare, Gazz. chim. ital. 1885, 15, 406; Zincke and Bindewald, Ber. 1884, 17, 3031; Zincke and Rathgen, *ibid.* 1886, 19, 2484; Fischer and Wimmer, *ibid.* 1887, 20, 1579; Weinberg, *ibid.* 3172; Jacobson, *ibid.* 1888, 21, 415; Meldola and East, Trans. Chem. Soc. 1888, 53, 460; Meldola and Morgan, *ibid.* 1889, 55, 603; Goldschmidt and Rosell, Ber. 1890, 23, 496; Goldschmidt and Brubacher, *ibid.* 1891, 24, 2306; McPherson, Ber. 1895, 28, 2418; Farmer and Hantzsch, *ibid.* 1899, 32, 3100; Möhlau and Strohbach, *ibid.* 1900, 33, 805; Goldschmidt and Keppeler, *ibid.* 894; Möhlau and Kegel, *ibid.* 2873; Betti, Gazz. chim. ital. 1900, 30, ii. 164.

Pigment Fast Red HL (M.); **Helio Fast Red RL** (By.); **Lithol Fast Scarlet R, RPN** (B.); **Graphitol Fast Red GAERR** (O.); **Sitara Fast Red RL** (T. M.); *m*-Nitrotolueneazo-β-naphthol

$$NO_2{\cdot}C_7H_6{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$$

Prepared from diazotised *m*-nitro-*p*-toluidine and β-naphthol. Used only for lakes.

Literature.—E. P. 19100 of 1905; D. R. P. appl. F 20265; F. P. 357858.

Tuscaline Orange G (B.). Prepared from diazotised *m*-nitro-*o*-anisidine and β-naphthol is used in calico-printing and as a lake.

Sudan II (A.) (K.); **Cerotine Scarlet G** (C. J.); **Motl Red G** (T. M.); **Pyronal Red R** (D.); **Orange RR** (B. K.); **Insoluble Xylidine Ponceau** (P.); Xyleneazo-β-naphthol

$$C_6H_3(CH_3)_2{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$$

Prepared from diazotised xylidine and β-naphthol.

Carminaph Garnet (D. H.); **Cerotine Scarlet 2 R** (C. J.); **Oil Red Brown** (Farbwerk Ammersfoort); **Pigment Bordeaux N** (M.); **Autol Red** (B.); **Insoluble Naphthylamine Ponceau** (P.); α-Naphthaleneazo-β-naphthol

$$C_{10}H_7{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$$

Prepared from diazotised α-naphthylamine and β-naphthol. An insoluble paste used in printing. (*See* also **Naphthylamine Bordeaux.**

Azophosphine GO (M.). Chloride of *m*-trimethylaminobenzeneazoresorcinol

$$ClN(CH_3)_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(OH)_2$$

Prepared from diazotised *m*-aminophenyltrimethylammonium chloride and resorcinol. Solution in water is yellowish-red, and in sulphuric acid brownish-red. A similar dye is **Azophosphine BRO** (M.).

Literature.—E. P. 14494 of 1895; D. R. P. 87257; F. P. 249227; A. P. 626913.

New Phosphine G (C.); ω-Dimethylaminotolueneazoresorcinol

$$N(CH_3)_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(OH)_2$$

Prepared from diazotised *p*-aminobenzyldimethylamine and resorcinol. Gives a yellowish-brown solution in water and sulphuric acid.

Literature.—E. P. 22572 of 1892; D. R. P. 70678; F. P. 225968; A. P. 515100.

Tannin Orange R (C.); ω-Dimethylaminotolueneazo-β-naphthol

$$N(CH_3)_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$$

Prepared from diazotised *p*-aminobenzyldimethylamine and β-naphthol. A brown powder or a 50 p.c. paste. Sparingly soluble in water, with a brown colour. Gives a yellowish-brown solution in sulphuric acid.

Literature.—As for the preceding colour.

Azochromine (G.); Tetrahydroxyazobenzene $OH\cdot C_6H_4\cdot N_2\cdot C_6H_2(OH)_3$. Prepared from diazotised *p*-aminophenol and pyrogallol. Commercial product is a 30 p.c. paste, giving a dark-yellow solution in boiling water. With sulphuric acid it gives a brown solution.

Literature.—E. P. 11902 of 1893; D. R. P. 81109; F. P. 230937; A. P. 548460.

Diazine Black (K.); Safranineazophenol. Prepared from one of the varieties of safranine and phenol. Its solution in water is dark green-blue, and in sulphuric acid green.

Literature.—Mon. Sci. 1886, (iii.) 16, 984.

Indoine Blue R (B.) (G.); **Janus Blue** (M.); **Naphthindone** (C.); **Vac Blue** (H.); **Fast Cotton Blue B** (O.); **Indole Blue** (A.) (L.); **Diazine Blue** (K.); **Madras Blue P** (P.); **Indone Blue** (By.); **Fast Blue B** (T. M.); **Indogenin** (Delft Colour Works); Safranineazo-β-naphthol. Prepared from various safranines and β-naphthol. It gives a violet solution in water, and a greenish-brown in sulphuric acid.

Literature.—E. P. 4543 of 1891, 18769 of 1893, 3488 of 1895, 23985 of 1898; D. R. P. 61692, 85690, 85932, 91721, 92015, 105433, 108497; F. P. 212276, 246239, 250239, 283013, 285360; A. P. 524251, 524254; Walter, Aus der Praxis der Anilinfarbenfabrikation, 1903, 306 (where the preparation is described in detail).

Methyl Indone B, R (C.) is prepared from diazotised safranine and an aminonaphthol. The aqueous solution is blue, and that in sulphuric acid greenish-blue.

Literature.—D. R. P. appl. L 3377.

Azarine S (M.)

$$OH\cdot C_6H_2Cl_2\cdot NH\cdot N(SO_3\cdot NH_4)\cdot C_{10}H_6\cdot OH$$

4 : 6-Dichloro-2-aminophenol is diazotised and combined with β-naphthol, and the product is treated with ammonium bisulphite. It forms a yellow paste, giving a yellow solution in water and a magenta-red solution in sulphuric acid, giving a reddish-brown precipitate on dilution.

Literature.—E. P. 5767 of 1883; D. R. P. 29067; F. P. 159604; A. P. 302790, 306546.

Sulphamine Brown A (D.); **α-Naphthine Brown** (P.) is prepared by the action of diazotised α-naphthylamine on the sodium bisulphite compound of nitroso-β-naphthol. It dissolves in water to a brown, and in sulphuric acid to a green, solution. **Sulphamine Brown B** (D.) is made from β-naphthylamine; the aqueous solution is red, and that in sulphuric acid is violet.

Literature.—E. P. 11556 of 1893; D. R. P. 79583; F. P. 239100.

D. Sulphonic Acids of Hydroxyazo- Compounds.

1. MONOSULPHONIC ACIDS.

Chrysoïn (most firms); **Tropæoline O** (C.); **Resorcin Yellow** (A.) (B. K.) (K.) (T. M.) (H.) (Sch.); **Gold Yellow** (By.); **Acme Yellow** (L.); *p*-Sulphobenzeneazoresorcinol

$$HSO_3\cdot C_6H_4\cdot N_2\cdot C_6H_3(OH)_2$$

Produced by the action of diazotised sulphanilic acid on resorcinol in alkaline solution. Solution of colouring matter orange; substance dissolves in sulphuric acid with a yellow colour.

Literature.—Griess, Ber. 1878, 11, 2195; Witt, Trans. Chem. Soc. 1879, 35, 183.

Acid Alizarine Garnet R (M.); *p*-Sulphophenolazoresorcinol

$$HSO_3\cdot C_6H_3(OH)\cdot N_2\cdot C_6H_3(OH)_2$$

Similarly prepared from *o*-aminophenol-*p*-sulphonic acid and resorcinol. Solution in water or sulphuric acid is orange-brown.

Orange II (Most firms); **Mandarin G** (A.) (B. K.) (By.); **Gold Orange** (By.) (B. K.) (D.) (T. M.); **Orange Extra** (C.); **Orange A** (L.) (Sch.); **Orange P** (O.); **Orange G** (B. K.) (H.); **Acid Orange** (G.); *p*-Sulphobenzeneazo-β-naphthol $HSO_3\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH$. Prepared from diazotised sulphanilic acid and β-naphthol. Solution orange, becoming red on addition of sodium hydroxide. Solution in sulphuric acid red, becoming orange on dilution.

Literature.—Hofmann, Ber. 1877, 10, 1378; Griess, *ibid.* 1878, 11, 2198; Witt, *ibid.* 1879, 12. 259; Miller, *ibid.* 1880, 13, 268; Witt, Chem. Zeit. 1880, 4, 437; Mühlhäuser, Dingl. poly. J. 1887, 264, 181, 238; Paul, Zeitsch. angew, Chem. 1896, 9, 686 (the last two papers give details of the manufacture).

Orange R (I.) (C.) (D. H.) (B.) (Sch.); **Orange T** (K.) (T. M.); **Kermesin Orange** (L.) Sulpho-*o*-tolueneazo-β-naphthol

$$HSO_3\cdot C_7H_6\cdot N_2\cdot C_{10}H_6\cdot OH(\beta)$$

Homologous with the preceding, the diazotised sulphonic acid of *o*-toluidine being used instead of sulphanilic acid.

Literature.—The manufacture is described in the paper by Mühlhauser already referred to.

Lithol Rubine B (B.); **Permanent Red 4 B** (A.); **Pigment Rubine R** (A.); Sulpho-*p*-tolueneazo-β-hydroxy-3-naphthoic acid

$$HSO_3\cdot C_7H_6\cdot N_2\cdot C_{10}H_5(OH)\cdot CO_2H$$

Prepared by the action of diazotised *p*-toluidinesulphonic acid $(CH_3 : NH_2 : SO_3H = 1 : 4 : 3)$ on β-hydroxynaphthoic acid. A fiery red powder or paste used for making lakes.

Literature.—E. P. 11004 of 1903; D. R. P. 151205; F. P. 332145; A. P. 741029.

Azofuchsine B (By.); Tolueneazo-1 : 8-dihydroxynaphthalenesulphonic acid

$$CH_3\cdot C_6H_4\cdot N_2\cdot C_{10}H_4(OH)_2\cdot SO_3H$$

Prepared by the action of diazotised commercial toluidine on 1 : 8-dihydroxynaphthalene-4-sulphonic acid. Solution in water is bluish-red, and in sulphuric acid violet.

Literature.—E. P. 18517 of 1889; D. R. P. 54116; F. P. 203744; A. P. 466841, 468142.

Ponceau 4 GB (A.) (Lev.) (B K.); **Croceïne Orange** (By.) (B. K.) (K.) (P.); **Croceïne Orange Y** (Sch.); **Croceïne Orange GR** (T. M.); **Brilliant Orange G** (M.) (C. J.); **Orange GRX** (B.); **Pyrotine Orange** (D.); Benzeneazo-β-naphtholsulphonic acid $C_6H_5\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH(\beta)$. Prepared by the action of diazobenzene chloride on β-naphthol-6-sulphonic acid (Schäffer's acid) in alkaline solution. Solutions in water or sulphuric acid are orange-yellow.

Literature.—Griess, Ber. 1878, 11, 2197.

Orange GT (By.); **Orange RN** (C.); **Brilliant Orange O** (M.); **Brilliant Orange RO** (C. J.); **Croceïne Orange R** (By.) (T. M.); Tolueneazo-β-naphtholsulphonic acid

$$C_7H_7\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH(\beta)$$

Prepared by diazotising commercial toluidien and combining with Schäffer's β-naphtholmonosulphonic acid in alkaline solution. Orange aqueous solution gives an oily precipitate with acids. Dissolves in sulphuric acid with a magenta-red colour, giving an oily deposit on dilution.

Literature.—E. P. 623 of 1879; Ber. 1880, 13, 586.

Scarlet GR (A.); **Scarlet R** (By.); **Brilliant Orange R** (M.) (C. J.) (B. K.); **Orange L** (Lev.) (P.) (O.); **Xylidine Orange 2 R** (T. M.); **Orange N** (K.) (B.); **Ponceau 2 G** (B.). Homologous with the last; prepared from diazotised xylidine and Schäffer's acid. Dissolves in sulphuric acid with a red colour, becoming brown and precipitating on dilution.

Literature.—Levinstein, Ber. 1880, 13, 586.

Azococcine 2 R (A.); **Double Scarlet R** (Lev.); **Jute Scarlet** (D.); **Ponceau R for Jute** (B.); Xyleneazo-α-naphtholsulphonic acid

$$(CH_3)_2C_6H_3{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH(\alpha)$$

Prepared by the action of diazoxylene chloride (commercial xylidine diazotised) on α-naphthol-4-sulphonic acid in alkaline solution. Aqueous solution not precipitated by alkalis; when hot and concentrated deposits bronzy crystals on cooling. Dissolves in sulphuric acid with a reddish-violet colour, becoming brown and precipitating free acid on dilution.

Literature.—E. P. 2237 of 1883; D. R. P. 26012.

Cochineal Scarlet 4 R (Sch.). Isomeric with the preceding, α-naphthol-5-sulphonic acid being used instead of the 4-sulphonic acid. Dissolves in sulphuric acid with a magenta-red colour, giving a precipitate on dilution.

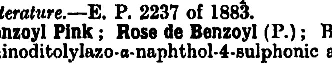
Azoeosine G (K.) (By.) (Lev.); **Cochineal Scarlet R** (D.); **Buffalo Flamine G** (Sch.); Anisoleazo-α-naphthol-4-sulphonic acid

$$CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$

Prepared from diazotised *o*-anisidine and α-naphthol-4-sulphonic acid. Gives a red solution in water and a carmine-red in sulphuric acid.

Literature.—E. P. 2237 of 1883.

Benzoyl Pink; **Rose de Benzoyl** (P.); Benzoylaminoditolylazo-α-naphthol-4-sulphonic acid



$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}\underset{CH_3}{\underset{|}{C_6H_4}}{\cdot}\underset{CH_3}{\underset{|}{C_6H_4}}{\cdot}N_2{\cdot}\underset{SO_3H}{\underset{|}{C_{10}H_6}}{\cdot}OH$$

Prepared from diazotised monobenzoyl-*o*-tolidine and α-naphthol-4-sulphonic acid. A brick-red paste, giving a cherry-red solution in water, and a bluish-red solution in sulphuric acid.

Literature.—D. R. P. 60332.

Double Ponceau R, 2 R, 3 R, 4 R (By.); α-Naphthaleneazo-α-naphthol-5-sulphonic acid $C_{10}H_7{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$. Prepared from diazotised α-naphthylamine and α-naphthol-5-sulphonic acid. Gives an orange-red solution in water, and a red in sulphuric acid.

Fast Red BT (By.) (Lev.) (D. H.) (B. K.); α-Naphthaleneazo-β-naphthol-6-sulphonic acid. Isomeric with the preceding. Prepared from diazotised α-naphthylamine and β-naphthol-6-sulphonic acid (Schäffer). Gives a red solution in water and a violet in sulphuric acid.

Literature.—E. P. 786 of 1878; D. R. P. 5411; F. P. 123148; A. P. 204799.

Pigment Scarlet G (M.); **Carboxybenzeneazo-β-naphthol-6-sulphonic acid**

$$CO_2H{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$

Prepared from diazotised anthranilic acid and Schäffer salt. A bronzy-red powder giving a yellowish-red aqueous solution and used for the preparation of lakes.

Literature.—D. R. P. 175828; F. P. 366110.

Fast Brown N (By.); **Chrome Brown RO** (M.); **Naphthylamine Brown** (B.); *p*-Sulphonaphthaleneazo-α-naphthol $HSO_3{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$. Prepared by the action of diazotised α-naphthylamine-4-sulphonic acid (naphthionic acid) on α-naphthol in alkaline solution. Colouring matter gives a reddish-brown solution, not changed by acids or alkalis. Dissolves in sulphuric acid with a reddish-violet colour.

Literature.—E. P. 786 of 1878; D. R. P. 5411, 87003; F. P. 123148; A. P. 204799.

Fast Brown 3 B (A.); Sulphonaphthalene-2-azo-α-naphthol $HSO_3{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$. Prepared by the action of diazotised β-naphthylamine-6-sulphonic acid on α-naphthol in alkaline solution.

Aqueous solution brownish-red, becoming violet with dilute acids and red with alkalis. Solution in sulphuric acid blue, giving reddish-violet precipitate on dilution.

Literature.—E. P. 3724 of 1882; D. R. P. 22547; F. P. 150503; A. P. 332829.

Permanent Orange R (A.); Chlorosulphobenzeneazo-β-naphthol

$$HSO_3{\cdot}C_6H_3Cl{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$$

Prepared from diazotised *m*-chloroaniline-*o*-sulphonic acid and β-naphthol. It is an orange paste used for making lakes.

Fast Orange O (M.); Nitrosulphobenzeneazo-β-naphthol

$$HSO_3{\cdot}C_6H_3(NO_2){\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$$

Prepared from diazotised *o*-nitroaniline-*p*-sulphonic acid and β-naphthol. An orange powder used for making lakes.

Literature.—E. P. 16409 of 1901; D. R. P. 129539; F. P. 313598; A. P. 714883.

Lake Red P (M.); Isomeric with the preceding. Prepared from diazotised *p*-nitroaniline-*o*-sulphonic acid and β-naphthol. It is a yellowish-red paste used for making calcium and barium lakes.

Literature.—E. P. 16409 of 1901; D. R. P. 128456; F. P. 313598; A. P. 714882.

Lake Red C (M.); Chlorosulphotolueneazo-β-naphthol $HSO_3{\cdot}C_7H_5Cl{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$. Prepared from diazotised 6-chloro-3-toluidine-4-sulphonic acid ($CH_3=1$) and β-naphthol. An orange paste used for making the red barium lake.

Literature.—E. P. 23831 of 1902; D. R. P. 145908; F. P. 328131; A. P. 733280.

Chrome Fast Cyanine G (I.), introduced into commerce in 1907, is prepared by the action of diazotised 1-amino-2-naphtholsulphonic acid on α-naphthol.

Eriochrome Blue Black B (G.); Sulphonaphtholazo-α-naphthol

$$HSO_3{\cdot}C_{10}H_5(OH){\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$$

Prepared by the action of diazotised 1-amino-β-naphthol-4-sulphonic acid on α-naphthol.[1] The blackish-violet aqueous solution on addition of hydrochloric acid becomes first reddish-brown, and then gives a brownish-black precipitate. With sodium hydroxide the solution becomes first blue and, on adding excess, finally red. The solution in sulphuric acid is blue, giving a violet-black precipitate on dilution.

Literature.—E. P. 15025 of 1904; D. R. P. 181326; F. P. 350055; Ital. P. 73530; Aust. P. 30630.

Eriochrome Black T (G.); Nitrosulphonaphtholazo-α-naphthol

$$NO_2\cdot C_{10}H_4(SO_3H)\cdot N_2\cdot C_{10}H_6\cdot OH$$

Prepared by the action of diazotised 8-nitro-1-amino-β-naphthol-4-sulphonic acid on α-naphthol. The reddish-brown aqueous solution gives a violet-brown precipitate with hydrochloric acid, and, with sodium hydroxide, becomes first deep-blue and then red. The solution in sulphuric acid is blackish-blue, giving a brown precipitate on dilution.

Literature.—E. P. 15982 of 1904; D. R. P. 169683; F. P. 350071; Ital. P. 73531; Aust. P. 127191.

Double Brilliant Scarlet G (A.) (Lev.) (K.) (T. M.) (A.); **Scarlet for silk** (M.); **Double Scarlet** (D.). Prepared from β-naphthylamine-6-sulphonic acid and β-naphthol. Aqueous solution gives brown precipitate with dilute acids. Dissolves in sulphuric acid with a red colour, giving a brown precipitate on dilution.

Literature.—E. P. 3724 of 1882; D. R. P. 22547; F. P. 150503; A. P. 332829.

Fast Red conc. (Sch.); **Fast Red A** (B.) (C. J.) (Lev.) (B. K.) (By.) (Claus & Co.) (L.) (K.) (D.) (T. M.) (O.); **Roccelline** (D. H.) (B. K.) (C.) (I.) (G.) (P.) (K. S.) (T. M.) (Central Dyestuff and Chemical Co.); **Fast Red AV** (B.); **Fast Red O** (M.); **Cardinal Red** (H.); **Rubidine** (B. K.); Sulphonaphthaleneazo-β-naphthol

$$HSO_3\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_6\cdot OH$$

Prepared by the action of diazotised naphthionic acid on β-naphthol in alkaline solution. Substance dissolves in hot water with a reddish-brown colour; concentrated solution when rapidly cooled solidifying to a brown gelatinous mass. Soluble in sulphuric acid with a violet colour, becoming brown and giving a precipitate of the free acid on dilution. The corresponding colouring matter from α-naphthylamine-5-sulphonic acid is called **Brilliant Fast Red G** (B.).

Literature.—E. P. 786 of 1878; D. R. P. 5411; F. P. 123148; A. P. 204799; Griess, Ber. 1878, 11, 2199; 1879, 12, 1364.

Acid Ponceau (D. H.) (K. S.); **Ponceau for Silk** (P.); **Ponceau S for silk** (I.); **Ponceau G for Silk** (K.); **Scarlet for Silk** (B.); Sulpho-β-naphthaleneazo-β-naphthol

$$HSO_3\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_6\cdot OH$$

Prepared by sulphonating β-naphthylamine, diazotising the mixed isomeric sulphonic acids, and combining with β-naphthol in alkaline solution. Aqueous solution gives a brown precipitate with dilute acids. Dissolves in sulphuric acid with a red colour, becoming brown and precipitating on dilution.

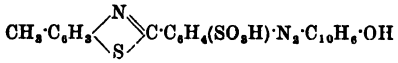
Lithol Red R (B.); Sulphonaphthaleneazo-β-naphthol $HSO_3\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_6\cdot OH$. Prepared by the action of diazotised β-naphthylamine-1-sulphonic acid on β-naphthol. The commercial product is a paste which is only very sparingly soluble even in hot water. It is used exclusively in the manufacture of lakes.

Literature.—E. P. 25511 of 1899; 4859 of 1909; 7922 of 1910; D. R. P. 112833; F. P. 297330; A. P. 650757.

Lake Bordeaux B (M.). Prepared from the same diazo- compound as the preceding and β-hydroxynaphthoic acid. It is a bordeaux-red paste used for making lakes.

Literature.—E. P. 7351 of 1907; D. R. P. 205080; F. P. 385570; A. P. 858065.

Clayton Cloth Red (Cl. Co.); **Stanley Red** (Cl. Co.); **Titan Scarlet** (H.); Sulphobenzenylaminothiocresolazo-β-naphthol



$$CH_3\cdot C_6H_3\overset{N}{\underset{S}{\langle\rangle}}C\cdot C_6H_4(SO_3H)\cdot N_2\cdot C_{10}H_6\cdot OH$$

Prepared by the action of diazotised dehydrothio-*p*-toluidinesulphonic acid on β-naphthol. The commercial product is the ammonium salt. Forms a reddish-brown solution in water, and a violet-red with sulphuric acid.

Literature.—E. P. 18901 of 1889; D. R. P. 51331.

Acid Alizarine Violet N (M.); **Palatine Chrome Violet** (B.); **Anthracene Chrome Violet B** (C.); **Ortho Cerise B** (A.); **Copper Red N** (M.); Sulphophenolazo-β-naphthol

$$OH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_{10}H_6\cdot OH$$

Prepared from diazotised 2-aminophenol-4-sulphonic acid and β-naphthol. Aqueous solution is dark bordeaux-red, and solution in sulphuric acid is magenta-red.

Literature.—D. R. P. 78409; D. R. P. appl. A 7938; F. P. 310508.

Acid Alizarine Black R (M.); Nitrosulphophenolazo-β-naphthol

$$OH\cdot C_6H_2(NO_2)(SO_3H)\cdot N_2\cdot C_{10}H_6\cdot OH$$

Prepared from diazotised 6-nitro-2-aminophenol-4-sulphonic acid and β-naphthol. Aqueous solution is brownish-violet, and solution in sulphuric acid is reddish-violet.

Literature.—E. P. 2772 of 1900; D. R. P. 143892; F. P. 300011; A. P. 667935.

Anthracene Chrome Black (C.); Sulphonaphtholazo-β-naphthol

$$HSO_3\cdot C_{10}H_5(OH)\cdot N_2\cdot C_{10}H_6\cdot OH$$

Prepared by the action of diazotised 3-amino-β-naphthol-7-sulphonic acid (R.) on β-naphthol. Aqueous solution is red; hydrochloric acid gives a reddish-violet precipitate, and sodium hydroxide turns it bluish-violet. Solution in sulphuric acid is bluish-green, giving a reddish-violet precipitate on dilution.

Literature.—E. P. 28107 of 1897; D. R. P. 109932; F. P. 272620, 272621.

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[1] In the constitutional formula of this colouring matter, kindly communicated along with other information to the writer by the manufacturers, the azo- group is shown attached to the 2- position of the α-naphthol, although the 4- position is unoccupied. The combination is probably effected in presence of very concentrated alkali hydroxide. Other examples of this ortho- combination are known, both in the benzene and naphthalene series. (Compare Michel and Grandmougin, Ber. 1893, 26, 2353; Bamberger, *ibid.* 1900, 33, 3188; Bamberger and Meimberg, *ibid.* 1895. 28, 1889; Bamberger, *ibid.* 848: D. R. P. 14443.)

Palatine Chrome Black 6 B (B.); **Eriochrome Blue Black R** (G.); **Salicin Black** (K.); **Acid Alizarin Blue Black A** (M.); **Diamond Blue Black EB** (By.); **Anthracene Blue Black BE** (C.); **Chrome Fast Black PW** (I.); **Chrome Blue N** (P.). Isomeric with the preceding. Prepared from diazotised 1-amino-β-naphthol-4-sulphonic acid and β-naphthol. Blue aqueous solution gives yellowish-brown precipitate with hydrochloric acid, and turns first blue and then red with sodium hydroxide. Solution in sulphuric acid is dark-blue, giving a blackish-brown precipitate on dilution.

Literature.—E. P. 27372 of 1903; 4997 and 15025 of 1904; D. R. P. 156440, 160536, 181326, 171024, 188645, 190693, 181714, 189175; D. R. P. appl. G 21484; F. P. 338819, 350055; A. P. 770177.

Salicin Black UL (K.) is the zinc sodium salt of the above, and is prepared by diazotising 1-amino-β-naphthol-4-sulphonic acid with zinc nitrite and combining the diazo-compound with β-naphthol in concentrated alkaline solution.

Literature.—E. P. 23034 of 1905; 22200 of 1909; D. R. P. 175593, 195228; F. P. 353786; A. P. 807422; Tomioka, J. Soc. Chem. Ind. 1917, 36, 1043.

Eriochrome Black A (G.); Nitrosulphonaphtholazo-β-naphthol

$$NO_2\cdot C_{10}H_4(SO_3H)(OH)\cdot N_2\cdot C_{10}H_6\cdot OH.$$

Prepared from diazotised 8-nitro-1-amino-β-naphthol-4-sulphonic acid and β-naphthol. Dark-blue aqueous solution gives a reddish-brown precipitate with hydrochloric acid, and becomes cherry-red with sodium hydroxide. Solution in sulphuric acid is dark-violet blue, giving a brown precipitate on dilution.

Literature.—E. P. 15982 of 1904; D. R. P. 169683; F. P. 350071; A. P. 790363; Ital. P. 73531; Aust. P. 27191.

Diamond Black PV (By.); Sulphophenolazo-1 : 5-dihydroxynaphthalene

$$OH\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_{10}H_5(OH)_2$$

Prepared from diazotised *o*-aminophenol-*p*-sulphonic acid and 1 : 5-dihydroxynaphthalene. The azo- group enters the 2-position in the latter component. Bluish-red aqueous solution gives a dark-red precipitate with hydrochloric acid. Solution in sulphuric acid is blackish-green, giving a reddish precipitate on dilution.

Literature.—E. P. 18139 and 18569 of 1902; Fischer, J. pr. Chem. 1917, [ii.] 95, 261.

Azo Acid Blue (M.) (By.); **Ethyl Acid Blue RR** (B.). Is prepared by the action of diazotised *p*-nitroaniline on 1 : 8-dihydroxynaphthalene-4-sulphonic acid, reducing the nitro- group and alkylating the product, or by the action of diazotised dialkyl-*p*-phenylenediamine on the sulphonic acid. It gives a blue-violet solution in water and a reddish-violet in sulphuric acid.

Literature.—E. P. 8270 of 1892; D. R. P. 70885, 77169; F. P. 221363; A. P. 567615.

Milling Yellow (Lev.) (D.) (L.); **Chrome Yellow D** (By.); **Anthracene Yellow BN** (C.); **Mordant Yellow** (B.) (M.); **Chrome Fast Yellow R** (A.); **Salicin Yellow D** (K.); **Alizarol Yellow** (Sch.); Sulphonaphthaleneazosalicylic acid

$$HSO_3\cdot C_{10}H_6\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH$$

Prepared by the action of diazotised β-naphthylamine-6-(or 5-)-sulphonic acid on salicylic acid. Solution in water is yellow, and in sulphuric acid yellowish-red.

Literature.—F. P. 206755.

Oriol Yellow (G.); **Cotton Yellow R** (B.); **Alkali Yellow** (D.). Prepared by the action of diazotised dehydrothio-*p*-toluidinesulphonic acid or primuline on salicylic acid. Gives an orange-yellow solution in water, and a scarlet-red with sulphuric acid.

Literature.—D. R. P. 48465; F. P. 192628; A. P. 398990.

Eriochrome Phosphine R (G.); Nitrosulphobenzeneazosalicylic acid

$$NO_2\cdot C_6H_3(SO_3H)\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH$$

Prepared by the action of diazotised *p*-nitroaniline-*o*-sulphonic acid on salicylic acid. Yellowish-orange aqueous solution becomes pale orange with hydrochloric acid, and blue-red with sodium hydroxide. Solution in sulphuric acid is yellowish-orange giving a pale-yellow precipitate on dilution.

Literature.—D. R. P. 226242.

2. Disulphonic Acids.

Chrome Brown RR (G.); Disulphophenolazopyrogallol

$$OH\cdot C_6H_2(SO_3H)_2\cdot N_2\cdot C_6H_2(OH)_3$$

Prepared by the action of diazotised *p*-aminophenol-2 : 6-disulphonic acid on pyrogallol. Solution in water is yellow, and in sulphuric acid brown.

Literature.—E. P. 11902 of 1893; D. R. P. 81109; F. P. 230937; A. P. 548460.

Orange G (A.) (M.) (B.) (P.) (C. J.) (T. M.) (Sch.) (K.) (O.) (Central Dyestuff and Chemical Co.); **Orange GG** (C.) (B. K.) (D.); **Orange GG in Crystals** (Sch.); **Fast Light Orange G** (By.); Benzeneazo-β-naphtholdisulphonic acid

$$C_6H_5\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH(\beta)$$

Produced by the action of diazobenzene chloride on β-naphthol-6 : 8-disulphonic acid (G-salt) in alkaline solution. Solution not precipitated by alkali; dissolves in sulphuric acid with an orange colour, undergoing no change on dilution.

Literature.—E. P. 1715 of 1878; D. R. P. 3229; F. P. 124811; A. P. 251162.

Crystal Scarlet 6 R (C.) (M.) (By.) (B. K.); **Crystal Ponceau** (A.) (K.) (B.) (D.) (L.) (P.); **Ponceau 6 R** (T.M.); α-Naphthaleneazo-β-naphthol-6 : 8-disulphonic acid (G-acid). Produced by the action of diazotised α-naphthylamine upon β-naphthol-6 : 8-disulphonic acid in alkaline solution.

Literature.—E. P. 816 of 1884; D. R. P. 36491; A. P. 332528.

Ponceau 2 G (B.) (M.) (B. K.); **Brilliant Ponceau GG** (C.); **Orange R** (H.). Isomeric with Orange G. Prepared by the action of diazobenzene chloride upon β-naphthol-3 : 6-disulphonic acid (R-salt). Properties similar to those of the preceding compound; colour slightly redder in shade.

Literature as for Orange G.

Azocoralline L (D.); **Azogrenadine L** (By.); *p*-Acetylaminobenzeneazo-β-naphthol-3 : 6-disulphonic acid

$$CH_3\cdot CO\cdot NH\cdot C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH$$

Prepared by the action of diazotised acetyl-*p*-phenylenediamine on β-naphthol-3 : 6-disulphonic acid (R-salt). Solution in water is orange-red, and in sulphuric acid yellowish-red.

Literature.—Nietzki, Ber. 1884, 17, 344.

Acid Alizarine Red B (M.); **Palatine Chrome Red B** (B.); Carboxybenzeneazo-β-naphthol-3 : 6-disulphonic acid

$$CO_2H{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$$

Prepared from diazotised anthranilic acid and R-salt. It gives a yellowish-red aqueous solution, and a red solution in sulphuric acid. In the form of a lake it is known as **Pigment Scarlet 3 B** (M.).

Literature.—E. P. 23830 of 1902; D. R. P. 141257; F. P. 328128; A. P. 757109.

Ponceau R, 2 R, G and **GR** [1] (A.) (B.) (M.) (By.) (B. K.) (O.) (P.) (L.) (K. S.) (T. M.) (Lev.) (C.) (C. J.); **Brilliant Ponceau R** (T. M.); **Scarlet 2 R** (H.) (Calco Chemical Co.); Xyleneazo-β-naphthol-3 : 6-disulphonic acid

$$C_8H_9{\cdot}N_2{\cdot}C_{10}H_4(SO_3)H_2{\cdot}OH(\beta)$$

Produced by the action of diazotised xylidine (chiefly meta-) on β-naphthol-3 : 6-disulphonic acid (R-salt). Properties similar to those of Orange G. Colour a distinct scarlet; aqueous solution not precipitated by alkali; an amorphous precipitate by calcium or barium chloride. Soluble with a red colour in sulphuric acid, becoming brown and precipitating on dilution.

Literature.—E. P. 1715 of 1878; D. R. P. 3229; F. P. 124811; A. P. 210233.

Ponceau 3 R (A.) (B.) (M.) (C. J.) (K.) (By.) (L.) (O.); **Ponceau 4 R** [2] (A.); **Ponceau 3 R 56** (Sch.); Cumeneazo-β-naphthol-3 : 6-disulphonic acid

$$C_9H_{11}{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH(\beta)$$

Produced by the action of diazocumene chloride (from ψ-cumidine) on R-salt. Properties as above; colour of a redder shade than the last.

Literature.—*See* above, and A. P. 251163.

Bordeaux B (H.) (A.) (M.) (B. K.) (Calco Chemical Co.); **Fast Red B** (B.) (B. K.) (L.); **Fast Red P extra** (By.); **Bordeaux BL** (C.); **Bordeaux R extra** (M.); **Bordeaux G** (D.); **Bordeaux R** (T. M.); **Cerasine** (P.); **Cerasine R** (D. H.); **Archelline 2 B** (Lev.); **Azo Bordeaux** (Sch.); α-Naphthaleneazo-β-naphthol-3 : 6-disulphonic acid

$$C_{10}H_7{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$$

Prepared from diazotised α-naphthylamine and R-salt. Solution in water is magenta-red, and in sulphuric acid blue, becoming magenta-red on dilution.

Literature.—E. P. 1715 of 1878; D. R. P. 3229; F. P. 124811; A. P. 251164.

Coccinine B, C (M.)

$$CH_3{\cdot}O{\cdot}C_6H_3(CH_3){\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$$

Prepared from diazotised 3-amino-4-cresol methyl ether and R-salt. Gives a cherry-red solution in water or sulphuric acid.

Literature.—E. P. 4914 of 1878; D. R. P. 7217; F. P. 124811.

Sorbine Red (B.); **Azogrenadine S** (By.); **Lanafuchsine** (various marks) (C.); **Azo Acid Red B** (M.); **Wool Red 8B** (O.); *p*-Acetylaminobenzeneazo-α-naphthol-3 : 6-disulphonic acid

$$CH_3{\cdot}CO{\cdot}NH{\cdot}C_4H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$$

Prepared by the action of diazotised acetyl-*p*-phenylenediamine on α-naphthol-3 : 6-disulphonic acid. Aqueous solution is currant-red, and in sulphuric acid fiery red.

Literature.—Chem. Zeit. 1900, 24, 493; Zeitsch. Farben. Ind. 1902, 26, 223.

Palatine Scarlet A (B.); **Cochineal Scarlet PS** (By.); **Nassoira Scarlet O** (M.); **Brilliant Wool Scarlet** (K.); **Brilliant Cochineal 2 R, 4 R** (C.); *m*-Xyleneazo-α-naphthol-3 : 6-disulphonic acid $C_8H_9{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$. Prepared from diazotised *m*-xylidine and α-naphthol-3 : 6-disulphonic acid. Solution in water is scarlet-red, and in sulphuric acid bluish-red.

Literature.—D. R. P. appl. G 3636.

XL Carmoïsine 6 B (H.); *m*-Xyleneazodihydroxynaphthalene-3 : 6-disulphonic acid $C_8H_9{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH)_2$. Prepared by the action of diazotised *m*-xylidine on 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid (chromatrope acid).

Eosamine B, G (A.); Methoxytolueneazo-α-naphthol-3 : 8-disulphonic acid

$$CH_3{\cdot}O{\cdot}C_7H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$$

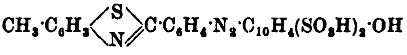
Prepared from diazotised *m*-amino-*p*-cresol methyl ether and α-naphthol 3 : 8-disulphonic acid. Solution in water is bluish-red, and in sulphuric acid violet-blue.

Literature.—Chem. Ind. 1896, 19, 8.

Palatine Red A (B.); **Naphthorubin O** (M.); α-Naphthaleneazo-α-naphthol-3 : 6-disulphonic acid $C_{10}H_7{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$. Prepared from diazotised α-naphthylamine and α-naphthol-3 : 6-disulphonic acid. Bluish-red solution in water, and blue in sulphuric acid.

Literature.—E. P. 15716 of 1885; D. R. P. 38281.

Direct Rose G (K. S.); **Erika 2 GN** (A.):

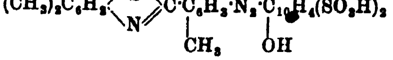


Prepared from diazotised dehydrothio-*p*-toluidine and α-naphthol-3 : 8-disulphonic acid (ε-acid). Cherry-red aqueous solution gives a scarlet-red precipitate with hydrochloric acid, and a bluish-red one with sodium hydroxide. Solution in sulphuric acid is dark-bluish red, giving a scarlet-red precipitate on dilution.

Geranine 2 B, G (By.); **Brilliant Geranine B, 2 BN, 3 B** (By.). These dyes are prepared from the same diazo- compound as the preceding, combined with α-naphthol-4 : 8-disulphonic acid (2 B), α-naphthol-3-sulphonic acid (G), or 1 : 8-dihydroxynaphthalene-4-sulphonic acid (Brilliant Geranine). The aqueous solution is red, and that in sulphuric acid is violet-red (2 B and G) or blue (Brilliant Geranine).

Literature.—D. R. P. 73251, 73340.

Erika B extra, BN (Lev.) (L.) (A.); Methylbenzenylaminothioxylenolazo-α-naphthol-3 : 8-disulphonic acid



Prepared from diazotised dehydrothio-*m*-xylidine and α-naphthol-3 : 8-disulphonic acid Solution in water or sulphuric acid is red.

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[1] **G GR** and **Brilliant Ponceau G** (C) are made from crude xylidine and crude R-salt, **R** from crude xylidine and **2 R** from *m*-xylidine and pure R-salt.

[2] **3 R** is made from crude cumidine and **4 R** from pure ψ-cumidine.

Literature.—E. P. 17333 of 1888; D. R. P. 63951; F. P. 194406; A. P. 418657; Anschütz and Schultz, Ber. 1889, 22, 583.

Erika G extra, GN (A.) (Lev.); **Erika 4 GN** (A.). Is isomeric with the preceding, being prepared from β-naphthol-6 : 8-disulphonic acid (G-acid), and has similar reactions.

Literature.—Ber. 1889, 22, 585.

Azocochineal (By.); Anisoleazo-α-naphthol-4 : 8-disulphonic acid

$$CH_3{\cdot}O{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$$

Prepared from diazotised *o*-anisidine and α-naphthol-4 : 8-disulphonic acid. Solution in water and sulphuric acid is red.

Literature.—E. P. 15775 and 15781 of 1885; D. R. P. 40571; F. P. 173083, 173084.

Chromotrope 2 R (M.); **XL Carmoisine R** (H.); Benzeneazo 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid

$$C_6H_5{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH)_2$$

Produced from diazotised aniline and 1 : 8-dihydroxynaphthalene - 3 : 6 - disulphonic acid. Gives in water a magenta-red, and in sulphuric acid a ruby-red solution.

Literature.—E. P. 9258 of 1890; D. R. P. 69095; F. P. 206439, 212607; A. P. 458283.

Chromotrope 2 B (M.); *p*-Nitrobenzeneazo-1 : 8 - dihydroxynaphthalene - 3 : 6 - disulphonic acid $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH)_2$. Prepared by the action of diazotised *p*-nitroaniline on 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid. Solution in water is yellowish-red, and in sulphuric acid dark-violet.

Literature.—As under Chromotrope 2R.

Victoria Violet 4 BS (M.) (By.); **Domingo Violet A** (L.); **Ethyl Acid Violet S 4 B** (B.); **Azo Wool Blue** (C.); *p*-Aminobenzeneazo-1 : 8-dihydroxynaphthalene - 3 : 6 - disulphonic acid $NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH)_2$. Prepared by the alkaline reduction of chromotrope 2 B or by eliminating the acetyl- group from chromotrope 6 B (*see* below). It gives a dark-violet solution in water, and a bluish-red in sulphuric acid. Similar colouring matters are **Victoria Violet 8 BS** (M.), **Victoria Violet 5 B** (By.), and **Victoria Violet L** (I.).

Literature.—E. P. 8270 of 1892; D. R. P. 70885, 73321; F. P. 221363, 226690.

Chromotrope 6 B (M.); **XL Fuchsine 6 B** (H.); **Fast Acid Red EBB** (L.); *p*-Acetylaminobenzeneazo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid

$$CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH)_2$$

Prepared by the action of diazotised acetyl-*p*-phenylenediamine on 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid. Solution in water is violet-red, and in sulphuric acid ruby-red.

Literature.—D. R. P. 75738.

Chromotrope 10 B (M.); Naphthaleneazo 1 : 8-dihydroxynaphthalene-3 : 6 disulphonic acid

$$C_{10}H_7{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH)_2$$

Prepared from diazotised α-naphthylamine and the above acid. Violet solution in water, and greenish-blue in sulphuric acid.

Literature.—As under Chromotrope 2 R.

Chromazone Red A (G.); Benzaldehydeazo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid $CHO{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH)_2$. Produced from diazotised *p*-aminobenzaldehyde and 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid. Solution in water is red, and in sulphuric acid blue.

Literature.—E. P. 13744 of 1896; D. R. P. 85233; F. P. 248517.

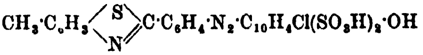
Chromazone Blue R (G.); Phenylethylhydrazone of the preceding colouring matter

$$C_6H_5(C_2H_5)N\,N:CH{\cdot}C_6H_4{\cdot}N_2\,C_{10}H_3(SO_3H)_2(OH)_2$$

Prepared either by condensing chromazone red with *as*-phenylethylhydrazine or by the action of diazotised *p*-aminobenzylidenephenylethylhydrazone on 1 : 8-dihydroxy-3 : 6-disulphonic acid. Solution in water is blue-violet, and in sulphuric acid blue-red.

Literature as above.

Diamine Rose (various marks); **Dianil Rose BD** (M.); Benzenylaminothiophenolazochloronaphtholdisulphonic acid



$$CH_3{\cdot}C_6H_3{<}\overset{S}{\underset{N}{}}{>}C{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4Cl(SO_3H)_2{\cdot}OH$$

Prepared from diazotised dehydrothio-*p*-toluidine and 8-chloro-α-naphthol-3 : 6-disulphonic acid. Magenta-red solution in water, and reddish-violet in sulphuric acid.

Literature.—E. P. 1920 and 9441 of 1894; D. R. P. 79055, 82285, 96768, 99227; F. P. 235271; A. P. 535037.

Fast Acid Fuchsine B (By.); **Fast Acid Fuchsine G** (B.K.); Benzeneazo-1 8: -aminonaphthol 3 : 6-disulphonic acid

$$C_6H_5{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2$$

Prepared from diazotised aniline and 1 : 8-aminonaphthol-3 : 6-disulphonic acid (H-acid) in alkaline solution. Solution in water or sulphuric acid is magenta-red.

Literature.—E. P. 13343 of 1890; D. R. P. 62368, 70031; F. P. 210033.

Tolane Red B (K.); Benzeneazo-1 : 8-aminonaphthol-4 · 6-disulphonic acid. Isomeric with the preceding. Prepared from diazotised aniline and 1 : 8-aminonaphthol-4 : 6-disulphonic acid (K-acid). Solution in water or sulphuric acid is magenta-red.

Literature.—E. P. 515 of 1894; D. R. P. 99164; A. P. 563383.

Amidonaphthol Red G (M.); **Brilliant Acid Carmine 2 G** (O.); **Azo Phloxine 2 G** (By.); Benzeneazo-1 : 8-acetylaminonaphthol-3 : 6-disulphonic acid

$$C_6H_5{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH{\cdot}CO{\cdot}CH_3$$

Prepared from diazotised aniline and acetyl H-acid in alkaline solution. Scarlet-red solution in water, and red solution in sulphuric acid.

Literature.—E. P. 26457 of 1905; D. R. P. 180089; F. P. 348426.

Amido Naphthol Red 6 B (M.); **Brilliant Acid Carmine 6 B** (O.). Prepared as the preceding, but *p*-aminoacetanilide is used instead of aniline. The solution in water or sulphuric acid is red.

Palatine Chrome Green G (B.); **Chrome Fast Green G** (I.); 4-Nitro-2-aminophenol is diazotised and combined with H-acid. It gives a dark reddish-violet solution in water, and a reddish-violet in sulphuric acid.

Fast Sulphone Violet 5 BS (K. S.) is prepared by combining a diazo- compound with 1 : 8-

aminonaphthol-3 : 6- or -4 : 6-disulphonic acid in alkaline solution, and treating the product with *p*-toluenesulphonyl chloride, whereby the amino- group is transformed into the *p*-toluenesulphonylamino- group. Other dyestuffs of the same kind are **Brilliant Sulphone Red B** (K. S.) and **Fast Sulphone Violet 4 R** (K. S.).

Literature.—E. P. 22886 of 1899; D. R. P. 120081; F. P. 294325; A. P. 640989.

Azo Archil R. (A.); Benzeneazo-2-amino-8-naphthol-3 : 6-disulphonic acid (2 R- acid). Isomeric with fast acid fuchsine B (By.). Prepared from diazotised aniline and 2 R-acid. Solution in water or sulphuric acid is yellowish-red.

Literature.—D. R. P. appl. A 3710.

Azorubine (Wiescher & Co.) (O.) (Lev.) (Central Dyestuff and Chemical Co.); **Azorubine S** (A.) (Sch.); **Azorubine G** (T. M); **Azorubine A** (C.); **Azo Acid Rubine** (C. J.) (D.); **Azo Acid Rubine R** (K.); **Nacarat** (P.); **Fast Red C** (B.) (B. K.); **Carmoisine** (K. S.); **Carmoisine B** (By.); **Carmoïsine S** (H.); **Mars Red G** (B.); **Brilliant Crimson** (Cl. Co.); **Brilliant Carmoisine O** (M.); Sulpho-α-naphthaleneazo-α-naphthol-sulphonic acid

$$HSO_3{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$

Prepared by the action of diazotised naphthionic acid on α-naphthol-4-sulphonic acid in presence of alkali. Solution gives a red crystalline precipitate with calcium chloride; substance dissolves in sulphuric acid with a bluish-violet colour, becoming red on dilution. When used for after-chroming on wool the dyestuff is known as **Azochrome Blue R** (K.); **Chrome Blue R** (B.); **Chromotrope FB** (M.); **Omega Chrome Blue A** (K. S.).

Literature.—E. P. 2237 and 4237 of 1883; D. R. P. 26012, 66838, 67240.

Fast Red VR (By); isomeric with the preceding. Prepared from diazotised naphthionic acid and α-naphthol-5-sulphonic acid. Aqueous solution is bluish-red and gives a reddish-brown precipitate with hydrochloric acid. Substance dissolves in sulphuric acid with reddish-blue colour. When used for after-chroming on wool the dyestuff is known as **Azochrome Blue B** (K.); **Chromotrope F 4 B** (M.). **Diamond Blue 3 B** (By.) also belongs to this class.

Fast Red (B.) (K.) (By.) (B. K.) (T. M.) (D.) (O.); **Fast Red S** (M.) (D. H.); **Naphthol Red EB** (C.); **Naphthol Red GR** (B.); **Acid Carmoïsine B** (B. K.); **Fast Red** (Lev.) (A.) (C. J.) (P.); Sulpho-α-naphthaleneazo-β-naphtholsulphonic acid $HSO_3{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$. Isomeric with the preceding; prepared from diazotised naphthionic acid and β-naphthol-6-sulphonic acid. Aqueous solution claret-red; not precipitated by acids, dissolves in sulphuric acid with a violet colour, becoming red on dilution.

Literature.—E. P. 786 of 1878; D. R. P. 5411; F. P. 123148; A. P. 204799.

Croceïne Scarlet 3 BX (By.) (K.); **Coccine 2 B** (A.); **Scarlet OOO** (H.); **Acidol Coccine 2 B** (T. M.). Isomeric with the last; prepared from diazotised naphthionic acid and β-naphthol-8-sulphonic acid. Hot solution (concentrated) gives a crystalline magnesium salt on adding magnesium sulphate and allowing to cool; solution in sulphuric acid reddish-violet becoming yellowish-red on dilution.

Literature.—E. P. 2031 of 1881; D. R. P. 20402; A. P. 256376.

Double Scarlet Extra S (A.) (Lev.); **Double Brilliant Scarlet 3 R** (By.); **Double Brilliant Scarlet S** (K.); **Brilliant Ponceau 4 R** (By.); **Scarlet PR** (P.); **Scarlet 2 R extra conc.** (T. M.). Isomeric with the last; prepared from diazotised β-naphthylamine-6-sulphonic acid and α-naphthol-4-sulphonic acid

$$HSO_3{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$

Aqueous solution gives yellowish-brown precipitate with dilute acids. Dissolves in sulphuric acid with a red colour, becoming yellower on dilution.

Literature.—E. P. 3724 of 1882; D. R. P. 22547; F. P. 150503; A. P. 332829.

Azofuchsine G (By.); **Fast Fuchsine G** (Sch.); *p*-Sulphobenzeneazodihydroxynaphthalene-4-sulphonic acid

$$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(OH)_2{\cdot}SO_3H$$

Prepared from diazotised sulphanilic acid and 1 : 8-dihydroxynaphthalene-4-sulphonic acid. Solution in water is bluish-red, and in sulphuric acid violet. Analogous colours are **Azofuchsine S, 6 B,** and **GN extra** (By.).

Literature.—E. P. 18517 of 1889; D. R. P. 54116; F. P. 203744; A. P. 466841, 468142.

Crumpsall Yellow (Lev.); Disulphonaphthaleneazosalicylic acid

$$C_{10}H_{.}(SO_3H)_2{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}CO_2H$$

Produced by the action of diazotised β-naphthylamine-6 : 8-disulphonic acid on salicylic acid. Solution in water is yellow, and in sulphuric acid, orange-red.

Literature.—E. P. 12145 of 1894; D. R. P. 87483.

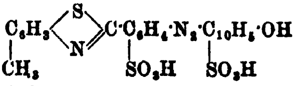
Lanacyl Blue BB (C.); Disulphohydroxynaphthaleneazoaminonaphthol

$$C_{10}H_4(SO_3H)_2(OH){\cdot}N_2{\cdot}C_{10}H_5(OH){\cdot}NH_2$$

Prepared from diazotised 1 : 8-aminonaphthol-3 : 6-disulphonic acid (H-acid) and 1 : 5-aminonaphthol in acetic acid solution (the azo- group attacks the ortho- position relative to the hydroxy- group). Solution in water is reddish or bluish-violet, and in sulphuric acid blue. To this group belong also **Lanacyl Blue R** and **Lanacyl Navy Blue B, 2 B,** and **3 B** (C.).

Literature.—E. P. 24134 of 1896; D. R. P. 95190; F. P. 260848.

Rosophenine 10 B (Cl. Co.); **Rosophenine Pink** (Cl. Co.); **Direct Scarlet B** (K.); **Thiazine Red R** (B.); **Benzoin Fast Red AE** (B. K.); Sulphobenzenylaminothiocresolazo-α-naphthol-4-sulphonic acid



$$\underset{\displaystyle CH_3}{\overset{|}{C_6H_3}}\left<\begin{matrix}S\\N\end{matrix}\right>C{\cdot}\underset{\displaystyle SO_3H}{\overset{|}{C_6H_4}}{\cdot}N_2{\cdot}\underset{\displaystyle SO_3H}{\overset{|}{C_{10}H_5}}{\cdot}OH$$

Prepared from diazotised dehydrothio-*p*-toluidinesulphonic acid and α-naphthol-4-sulphonic acid. Solution in water is crimson-red, and in sulphuric acid violet-red.

The corresponding colour from diazotised primuline is called **Rosophenine SG** (Cl. Co.); (D. R. P. 48465; F. P. 192628, 196988; A. P. 398990).

Thiazine Red G (B.). Prepared from diazotised primuline (sulphonic acid) and β-naphthol-6-sulphonic acid. Orange-red aqueous solution gives an orange-red precipitate with hydrochloric acid, and becomes dark with sodium hydroxide. Solution in sulphuric acid is blood-red, giving an orange precipitate on dilution.

The corresponding colour from diazotised dehydrothio-*p*-toluidinesulphonic acid is **Clayton Cloth Scarlet** (Cl. Co.); **Titan Pink 3 B** (H.); **Thiazine Red GN** (B.).

References as for rosophenine SG.

3. Trisulphonic Acids.

Azo Red A (C.); Sulpho-α-naphthaleneazo-α-naphthol-3 : 6-disulphonic acid

$$HSO_3\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH$$

Prepared by the action of diazotised naphthionic acid on α-naphthol-3 : 6-disulphonic acid. Aqueous solution red. Solution in sulphuric acid is blue, becoming violet and then red on dilution.

New Coccine (A.) (M.); **Brilliant Scarlet** (Lev.) (C.); **Croceine Scarlet 4 BX** (K.); **Victoria Scarlet 4 R** (T. M.); **Special Ponceau** (P.); **Cochineal Red A** (B.); **Brilliant Ponceau 4 R** (By.) (C.); **Brilliant Ponceau 5 R** (By.) (D.); **Ponceau 4 R** (B. K.); **Brilliant Scarlet S** (Sch.); **Scarlet 5 O** (H.); **Scarlet N** (Farbwerk Ammersfoort); Sulpho-α-naphthaleneazo-β-naphthol-6 : 8-disulphonic acid

$$HSO_3\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH$$

Prepared by the action of diazotised naphthionic acid on β-naphthol-6 : 8-disulphonic acid (G-salt). Aqueous solution red, not precipitated by acids. Dissolves in sulphuric acid with a red colour, becoming yellowish-red on dilution.

Literature.—E. P. 816 of 1884; D. R. P. 3229, 36491; F. P. 124811; A. P. 314938.

Fast Red D (B.) (O.); **Azo Acid Rubine 2 B** (D.) (B K.) (C. J.); **Cloth Red** (T. M.); **Bordeaux S** (A.) (Lev.); **Amaranth** (M.) (C.) (B. K.) (P.) (I.) (D. H.) (T. M.) (Lev.) (Central Dyestuff and Chemical Co.) (Ault and Wiborg Co.); **Naphthol Red O** (M.); **Naphthol Red S** (B.) (B K.); **Naphthol Red C** (C.); **Naphthylamine Red G** (By.); **Fast Red** (C. J.); **Fast Red NS** (By.); **Bordeaux DH** (D. H.); **Victoria Rubine O** (M.) (B K.); **Azo Rubine S** (K. S.); **Amaranth 107** (Sch.); **Acid Crimson** (H.); **Wool Red** (Sch.); **Wool Red extra** (K.); **Azo Red N extra** (L.). Isomeric with the preceding. Prepared from diazotised naphthionic acid and R-salt.

Literature.—D. R. P. 3229.

Chromotrope 8 B (M.); *p*-Sulphonaphthaleneazodihydroxynaphthalene-3 : 6-disulphonic acid

$$HSO_3\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2$$

Prepared by the action of diazotised naphthionic acid on 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid. Solution in water is violet-red, and in sulphuric acid indigo-blue. In addition to this and the other 'chromotrope' colours mentioned above, the marks S and 7 B also appear on the market, but their constitution has not yet been published.

Literature.—E. P. 9258 of 1890; D. R. P. 69095; F. P. 212607; A. P. 458283.

4. Tetrasulphonic Acids.

Ponceau 6 R (M.) (B.); *p*-Sulphonaphthaleneazo-β-naphtholtrisulphonic acid

$$HSO_3\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_3(SO_3H)_3\cdot OH$$

Prepared by the action of diazotised naphthionic acid on β-naphthol-3 : 6 : 8-trisulphonic acid. Solution in water is magenta-red, and in sulphuric acid violet.

Literature.—E. P. 2544 of 1882; D. R. P. 22038; F. P. 149249; A. P. 268506.

Heliopurpurine 4 BL (By.); Disulphonaphthaleneazo-α-naphthol-3 : 6-disulphonic acid

$$C_{10}H_5(SO_3H)_2\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH$$

Prepared from diazotised β-naphthylamine-3 : 6-disulphonic acid and α-naphthol-3 : 6-disulphonic acid. Used exclusively in the manufacture of lakes.

Literature.—Farber-Zeit. 1904, 15, 95.

Heliopurpurine 7 BL (By.). Isomeric with the preceding. Prepared by the action of diazotised β-naphthylamine-1 : 6-disulphonic acid on β-naphthol-3 : 6-disulphonic acid (R-salt). Used only for lakes.

Literature as above.

5. Pentasulphonic Acids.

Heliopurpurine GL (By.); Disulphonaphthaleneazo-β-naphthol-3 : 6 : 8-trisulphonic acid

$$C_{10}H_5(SO_3H)_2\cdot N_2\cdot C_{10}H_3(SO_3H)_3\cdot OH$$

Prepared from diazotised β-naphthylamine-3 : 6-disulphonic acid and β-naphthol-3 : 6 : 8-trisulphonic acid.

Use and literature as above.

E. Carboxylic Acids of Hydroxyazo- Compounds.[1]

Alizarine Yellow GG (M.) (I.); **Chrome Yellow R** (P.); **Alizarine Yellow G, 3 G** (Lev.); **Alizarine Yellow 3 G** (By.); **Mordant Yellow 2 G T** (B.); **Anthracene Yellow GG** (C.); **Alizarine Yellow G** (K. S.); *m*-Nitrobenzeneazosalicylic acid

$$NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH$$

Prepared from diazotised *m*-nitroaniline and salicylic acid. The commercial product (the free acid) is usually a yellow paste, insoluble in water, and giving an orange solution with sulphuric acid. The sodium salt is put on the market in the dry state as **Alizarine Yellow GGW** (M.) (Ault and Wiborg Co.).

Literature.—E. P. 17583 of 1887; D. R. P. 44170; F. P. 187821; A. P. 424019.

Alizarine Yellow R (M.) (C. R.) (By.); **Alizarine Orange R, 2 R** (Lev.); **Mordant Yellow 3 R** (B.); **Mordant Yellow PN** (Farbwerk Ammersfoort); **Orange R** (K. S.); **Milling Orange R** (L.); **Anthracene Yellow RN** (C.); **Metachrome Orange R** (A.) (Brotherton & Co.); **Chromoxanthine** (K. S.); **Terracotta R** (G.); **Chrome Orange** (P.). Isomeric with the last. Prepared from diazotised *p*-nitroaniline and salicylic acid. Comes on the market as a brown paste insoluble in water and giving an orange-yellow solution with sulphuric acid. This consists of the free acid; the sodium salt (soluble in water with an orange colour) is called **Alizarine Yellow RW** (M.) (Marden, Orth, and Hastings Corporation).

Literature.—Meldola, Chem. Soc. Trans. 1885, 47, 666; Bull. Mulhouse, 1892, 198; J. Soc.

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[1] Carboxylic acids containing also sulphonic acid groups are described under the corresponding sulphonic or disulphonic acids.

Chem. Ind. 1890, 9, 53; 1892, 11, 599; J. Soc. Dyers, 1889, 5, 106; E. P. 13920 of 1888; F. P. 193190; A. P. 431297.

Chrome Fast Yellow GG (A.); *o*-Anisoleazosalicylic acid $CH_3{\cdot}O{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH$. Prepared from diazotised *o*-anisidine and salicylic acid. In commerce as a bright-yellow paste or a yellow powder. Solution in hot water is greenish-yellow, and in sulphuric acid yellowish-brown.

Literature.—E. P. 12221 of 1895; D. R. P. 84772.

Azoalizarine Yellow 6 G (D. H.); **Alizarine Yellow 5 G** (M.); **Tartrachromine GG** (I.); *p*-phenetoleazosalicylic acid

$$C_2H_5{\cdot}O{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH$$

Prepared from diazotised *p*-phenetidine and salicylic acid. Solution in water is yellowish-brown, and in sulphuric acid brown-red.

Diamond Flavine G (By.); *p*-Hydroxydiphenylazosalicylic acid

$$OH{\cdot}C_{12}H_8{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH$$

Prepared by boiling the intermediate product from tetrazotised benzidine and one molecule of salicylic acid. In commerce as a yellowish-brown paste or powder which dissolves in water only after the addition of sodium acetate. Solution in sulphuric acid is blood-red. If the intermediate product is treated with sodium bisulphite, the product is known as **Dutch Yellow** (Farbwerk Ammersfoort); **Mordant Yellow GRO** (B.), which gives a yellow solution in water, and a bordeaux-red one in sulphuric acid (D. R. P. 68953).

Literature.—E. P. 11603 of 1891; D. R. P. 60373; F. P. 214756.

Diamond Yellow G (By.); *m*-Carboxybenzeneazosalicylic acid

$$CO_2H{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH$$

Prepared from diazotised *m*-aminobenzoic acid and salicylic acid. A greyish-yellow paste soluble in water (with addition of sodium acetate or carbonate) with a yellow colour. Gives a reddish-yellow solution with sulphuric acid.

Literature.—E. P. 8299 of 1889; D. R. P. 58271; F. P. 198521 (addition); A. P. 502368, 502369.

Lake Red D (M.); Carboxybenzeneazo-β-naphthol $CO_2H{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$. Prepared from diazotised anthranilic acid and β-naphthol. Orange-red paste used for lakes.

Literature.—E. P. 22781 of 1906; D. R. P. 189023; F. P. 373115; A. P. 878964.

Brilliant Lake Red R (M.); Benzeneazo-2-hydroxy-3-naphthoic acid

$$C_6H_5{\cdot}N_2{\cdot}C_{10}H_5(OH){\cdot}CO_2H$$

Prepared from diazotised aniline and β-hydroxynaphthoic acid. Used for making lakes

Literature.—Ber. 1893, 26, 2897.

F. Unclassified Monoazo- Colouring Matters.

Peri Wool Blue B, BG, G (C.). These colouring matters are produced by the action of diazotised nitroaminophenols on *peri*- derivatives of naphthalene.

III. DISAZO- COMPOUNDS.[1]

A. Primary Disazo- Colouring Matters.[2]

Leather Brown (O.):

$$NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_2(NH_2)_2{\cdot}N_2{\cdot}C_6H_4{\cdot}NH_2$$

Prepared by combining 2 mols. of *p*-diazoacetanilide with 1 mol. of *m*-phenylenediamine, and heating the product with strong hydrochloric acid. Commercial product is the monohydrochloride or the zinc chloride double salt. The brown aqueous solution becomes yellower on adding hydrochloric acid, and gives a brown precipitate with sodium hydroxide. The substance gives a brown solution in sulphuric acid, which becomes yellowish-brown on dilution.

Literature.—E. P. 11218 of 1891; D. R. P. 57429; A. P. 462414.

Terra Cotta F (G.); **Clayton Cotton Brown** (Cl. Co.):

$$P^{3}{\cdot}N_2{\cdot}C_6H_2(NH_2)_2{\cdot}N_2{\cdot}C_{10}H_6{\cdot}SO_3H$$

Prepared by combining first diazotised naphthionic acid and secondly diazotised primuline with *m*-phenylenediamine. Solution in water is brown, giving a brown precipitate with hydrochloric acid. Sulphuric acid dissolves colour to a reddish-violet solution, giving a brown precipitate on dilution.

Literature.—E. P. 1688 and 8215 of 1890; D. R. P. appl. G. 5870; F. P. 203439; A. P. 440288.

Cotton Orange R (B.):

$$P^{3}{\cdot}N_2{\cdot}C_6(NH_2)_2(SO_3H)_2{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H^{4}$$

Prepared by combining first diazotised primuline and secondly diazotised metanilic acid with *m*-phenylenediaminedisulphonic acid. The orange-red aqueous solution gives a reddish precipitate with hydrochloric acid. Solution in sulphuric acid is bright red, precipitating on dilution.

Literature.—E. P. 21753 of 1893; D. R. P. 76118; F. P. 231694; A. P. 524261.

Anthracene Acid Brown G (C.) (Marden, Orth, and Hastings Corporation):

$$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_2(CO_2H)(OH){\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2$$

Prepared by combining diazotised sulphanilic acid (1 mol.) and diazotised *p*-nitroaniline (1 mol.) with salicylic acid (1 mol.). Aqueous solution is reddish-brown, and that in sulphuric acid is bluish-green.

Literature.—E. P. 17590 of 1896; D. R. P. 95066; F. P. 258783.

Resorcin Brown (A.) (K.) (H.) (I.) (B. K.) (Sch.):

$$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_2(OH)_2{\cdot}N_2{\cdot}C_8H_9$$

Diazoxylene chloride is combined with resorcin yellow. Aqueous solution gives a brown precipitate with acids. Dissolves in sulphuric acid with a brown colour.

Literature.—D. R. P. 18861; A. P. 269359.

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[1] *See* also DISAZO- AND TETRAZO- COLOURING MATTERS.

[2] It will be sufficient to give the chemical formulæ of these disazo-compounds without giving their names in full.

[3] P=residue of primuline or dehydrothiotoluidine refers to sulphonic acid.

[4] According to Heumann (Die Anilinfarben und ihre Fabrikation) the formula is—

$$P{\cdot}N_2{\cdot}C_6H(NH_2)(SO_3H)_2{\cdot}NH{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H$$

Fast Brown G (A.); **Acid Brown** (D.) (P.); **Acid Brown G** (T. M.) (B. K.)

$$(HSO_3 \cdot C_6H_4 \cdot N_2)_2C_{10}H_5 \cdot OH(\alpha)$$

Prepared by the action of diazotised sulphanilic acid (2 mols.) on α-naphthol (1 mol.). Aqueous solution red-brown; violet precipitate with dilute acid. Sulphuric acid solution violet, becoming yellowish-brown on dilution.

Literature.—Krohn, Ber. 1888, 21, 3241.

Fast Brown (By.); **Resorcin Dark Brown** (B. K.): $(HSO_3 \cdot C_{10}H_6 \cdot N_2)_2C_6H_2(OH)_2$. Prepared by the action of diazotised naphthionic acid (2 mols.) on resorcinol (1 mol.). Brown aqueous solution gives a readily soluble precipitate with hydrochloric acid, and becomes cherry-red with sodium hydroxide. Solution in sulphuric acid is currant-red.

Literature.—D. R. P. 18861.

Palatine Black A (B.); **Wool Black 4 B** and **6 B** (A.); **Buffalo Black PY** (Sch.)

$$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_3(SO_3H)(OH)(NH_2) \cdot N_2 \cdot C_{10}H_7$$

Prepared by the action of diazotised sulphanilic acid (1 mol.) on 1 : 8-aminonaphthol-4-sulphonic acid in acid solution, and treating the product in alkaline solution with diazotised α-naphthylamine (1 mol.) in alkaline solution. Dark-blue aqueous solution becomes bluish-green with hydrochloric acid and pure blue with sodium hydroxide. The solution in sulphuric acid is blue, giving a dark-blue precipitate on dilution.

Literature.—E. P. 7713 of 1891 and 9894 of 1893; D. R. P. 71199, 91855; F. P. 213232; A. P. 590088, 593790.

Naphthol Blue Black S; **Naphthol Black 12 B** (C.); **Naphthol Blue Black B**; **Acid Black 16622** (L.); **Wool Black 6 G extra conc.** (T. M.); **Naphthalene Black 10 B** (P.); **Blue Black NB** (K.); **Coomassie Blue Black** (Lev.); **Amido Black 10 BO** (M.); **Amido Acid Black 10 B** (A.); **Naphthylamine Black 10 B** (By.); **Buffalo Black NB** (Sch.); **Agalma Black 10 B** (B.):

$$NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_2(SO_3H)_2(OH)(NH_2) \cdot N_2 \cdot C_6H_5$$

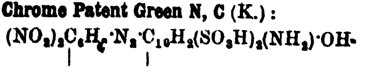
Prepared by the action of diazotised *p*-nitroaniline (1 mol.) on 1 : 8-aminonaphthol-3 : 6-disulphonic acid (H-acid) in acid solution, and treating the product in alkaline solution with diazotised aniline. The dark-blue aqueous solution gives a blue precipitate with hydrochloric acid. The solution in sulphuric acid is green, giving a blue precipitate on dilution.

Literature.—E. P. 1742 and 6972 of 1891; D. R. P. 65651; F. P. fourth addition to 201770; A. P. 480326.

Domingo Blue Black (various marks) (L.). Isomeric with the preceding, 1 : 8-aminonaphthol-3 : 5-disulphonic acid being used instead of H-acid. Mark B gives a violet aqueous solution, and a green solution in sulphuric acid.

Literature.—E. P. 19253 of 1895; D. R. P. appl. F 8626; A. P. 606438.

Chrome Patent Green N, C (K.):

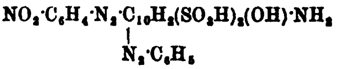


$$\begin{array}{l}(NO_2)_2C_6H_2 \cdot N_2 \cdot C_{10}H_2(SO_3H)_2(NH_2) \cdot OH\\ \qquad\;\; | \qquad\quad\;\; |\\ \qquad OH \qquad N_2 \cdot C_6H_5\end{array}$$

Prepared by the action of diazotised aniline (1 mol.) and diazotised picramic acid (1 mol.) on 1 : 8-aminonaphthol-4 : 6-disulphonic acid.

Literature.—E. P. 15074 of 1899; D. R. P. 110711; F. P. 291316.

Blue Black N (K.):



$$\begin{array}{l}NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_2(SO_3H)_2(OH) \cdot NH_2\\ \qquad\qquad\qquad\;\; |\\ \qquad\qquad\qquad N_2 \cdot C_6H_5\end{array}$$

Prepared by the action of diazotised *p*-nitroaniline (1 mol.) on 1 : 8-aminonaphthol-4 : 6-disulphonic acid in acid solution, and treating the product in alkaline solution with diazotised aniline.

Literature.—D. R. P. 108266; F. P. 271070; A. P. 563384, 613639.

Supramine Black BR (By.). The special base used in the preparation of this colouring matter is *p*-aminophenyl ether. Two mols. (or one of this and one of another base) are diazotised and combined with 1 : 8-aminonaphthol-4 : 6- or 3 : 6-disulphonic acid.

Literature.—F. P. 402546; A. P. 958830.

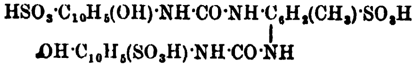
Janus Yellow R (M.).

$$N(CH_3)_3Cl \cdot C_6H_4 \cdot N_2 \cdot C_6H_2(OH)_2 \cdot N_2 \cdot C_6H_4 \cdot NO_2$$

Prepared by combining diazotised *m*-aminophenyltrimethylammonium chloride with *m*-nitrobenzeneazoresorcinol. Yellowish-brown aqueous solution gives a yellowish-brown precipitate. Solution in sulphuric acid is magenta-red, becoming yellow on dilution.

Literature.—E. P. 5119 of 1897; D. R. P. 93499, 95530, 99127, 100420; F. P. 264579; A. P. 623697.

Azidine Fast Scarlet GGS, 4 BS, 7 BS (C. J.). These dyes are prepared by the action of 2 mols. of a diazo- compound on the substance



$$\begin{array}{l}HSO_3 \cdot C_{10}H_5(OH) \cdot NH \cdot CO \cdot NH \cdot C_6H_2(CH_3) \cdot SO_3H\\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\;\; |\\ \quad OH \cdot C_{10}H_5(SO_3H) \cdot NH \cdot CO \cdot NH\end{array}$$

The brand **GGS** is made from diazotised *o*-toluidine (2 mols.), **4 BS** from diazotised *o*-toluidine (1 mol.), and diazotised β-naphthylamine (1 mol.), and **7 BS** from diazotised β-naphthylamine (2 mols.).

Literature.—E. P. 1781 of 1910; D. R. P. appl. J. 11718; F. P. 412138; A. P. (appl.) 541843.

Benzo Fast Scarlet GS, 4 BS, 8 BS, &c. (By.). These dyes are obtained by the action of 2 mols. of a diazo- compound on the urea produced by the action of carbonyl chloride on 2 mols. of 5-amino-α-naphthol-3-sulphonic acid (J-acid): *i.e.* $HSO_3 \cdot C_{10}H_5(OH) \cdot NH \cdot CO \cdot NH \cdot C_{10}H_5(OH) \cdot SO_3H$, or by treating azo- colouring matters from diazo- compounds and J-acid with carbonyl chloride or with carbon disulphide.

Literature.—E. P. 3615 of 1900; D. R. P. 122904, 126133, 126801, 128195, 132511, 133466; F. P. 297367; A. P. 653498, 662122, 675629, 675632.

B. Secondary Disazo- Colouring Matters.

Sudan III (A.); **Cerasine Red** (C.) (Barking Chemicals Co., Ltd.); **Fat Ponceau G** (K.); **Scarlet R** (C. J.); **Scarlet B Oil Soluble** (B. K.); **Moti Red 2 R** (T. M.); **Pyronal Red B** (D.); **Oil Red O** (Sch.):

$$C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta)$$

Prepared by the action of diazotised aminoazobenzene on β-naphthol. Insoluble in water; dissolves in sulphuric acid with a green colour.

becoming blue, and finally red and precipitating on dilution.

Literature.—Nietzki, Ber. 1880, 13, 1838; E. P. 5003 of 1879; D. R. P. 16483, 55779; F. P. 134802.

Ponceau 5 R (M.) (K.); **Erythrine P** (B.):

$$C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_3{\cdot}OH$$

Prepared by the action of diazotised aminoazobenzene on β-naphthol-3 : 6 : 8-trisulphonic acid in alkaline solution. Cherry-red aqueous solution gives a brown precipitate with hydrochloric acid, and becomes violet with sulphuric acid.

Literature.—E. P. 2544 of 1882; D. R. P. 22038; F. P. 149249; A. P. 268507.

Cloth Red G (By.); **Cloth Red R** (D.); **Silk Red R** (B.); **Fast Silk Red** (O.):

$$C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$

Prepared by the action of diazotised aminoazobenzene on α-naphthol-4-sulphonic acid in alkaline solution. Dissolves in sulphuric acid with a violet colour, giving a brownish-red precipitate on dilution.

Literature.—E. P. 2237 of 1883; D. R. P. 26012.

Croceine B (Sch.). The disulphonic acid corresponding with the preceding; produced by the action of diazotised aminoazobenzene on α-naphthol-4 : 8-disulphonic acid.

Literature.—E. P. 15775 and 15781 of 1885; D. R. P. 40571; F. P. 173083, 173084; A. P. 333037.

Croceine AZ (C.). Isomeric with the preceding. Prepared from α-naphthol-3 : 6-disulphonic acid. The solution in water is red, and in sulphuric acid reddish-violet.

Brilliant Croceine M (C.) (B K.) (O.); **Brilliant Croceïne 3 B** (By.); **Brilliant Croceine bluish** (M.); **Brilliant Croceine O** (K.); **Brilliant Croceïne, extra conc.** (T. M.); **Cotton Scarlet** (B.); **Ponceau BO extra** (A.); **Croceine 3 B** (P.); **Croceïne AZ** (K. S.); **Paper Scarlet** (M.):

$$C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$$

Prepared by the action of diazotised aminoazobenzene on β-naphthol-6 : 8-disulphonic acid. Dissolves in sulphuric acid with a reddish-violet, becoming first bluer and then red on dilution.

Literature.—E. P. 816 of 1884; D. R. P. 36491; F. P. 159998; A. P. 314939.

Azo Acid Violets (various marks) (By.) are prepared from diazotised aminoazobenzene (and similar compounds) and 1 : 8-dihydroxynaphthalene-4-sulphonic acid (or disulphonic acid).

Literature.—E. P. 3397 of 1890; 5984 of 1891; D. R. P. 57021, 64017.

Sudan IV (A.) (D.); **Oil Ponceau** (M.) (W.); **Cerotine Ponceau 3 B** (C. J.); **Fat Ponceau R** (K.); **Scarlet BBB Oil Soluble** (B. K.); **Red P 1566** (P.). (*See* also **Fast Azo Garnet**, p. 457.) $C_7H_7{\cdot}N_2{\cdot}C_7H_6{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$. Prepared from diazotised *o*-aminoazotoluene and β-naphthol. Insoluble in water, but soluble in alcohol or benzene with a bluish-red colour. Sulphuric acid gives a blue solution, which yields a red precipitate on dilution.

Cloth Red B (By.) (D.):

$$C_7H_7{\cdot}N_2{\cdot}C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$

Prepared by the action of diazotised *o*-aminoazotoluene on α-naphthol-4-sulphonic acid. The red aqueous solution gives a red precipitate with hydrochloric acid, and on adding sodium hydroxide to the solution it becomes violet. The solution in sulphuric acid is blackish-blue.

Literature.—E. P. 5003 of 1879; D. R. P. 16482.

Cloth Red G (O.); **Cloth Red G extra** (By.); **Cloth Red GA** (A.); **Acidol Cloth Red G** (T. M.):

$$C_7H_7{\cdot}N_2{\cdot}C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH(\beta)$$

Produced by the action of diazotised aminoazotoluene on β-naphthol-6-sulphonic acid. Dissolves in water with a red-brown colour giving a similarly coloured precipitate on addition of acid. Dissolves with a blue colour in sulphuric acid, giving a brownish-red precipitate on dilution.

Literature.—E. P. 5003 of 1879; D. R. P. 16482.

Cloth Red B (O.) (K.); **Cloth Red O** (M.); **Cloth Red BA** (A.); **Cloth Red BB** (D.); **Fast Bordeaux O** (M.); **Fast Milling Red B** (Lev.); **Wool Red B** (C.):

$$C_7H_7{\cdot}N_2{\cdot}C_7H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH(\beta)$$

Prepared by the action of diazotised aminoazotoluene on β-naphthol-3 : 6-disulphonic acid (R-salt). Aqueous solution red, becoming brownish on addition of hydrochloric acid. Dissolves in sulphuric acid with a blue colour, giving a brownish-red precipitate on dilution.

Literature as under preceding colour and E. P. 536 of 1880.

Cloth Red 3 G extra (By.); **Cloth Red 3 GA** (A.); **Cloth Red 3 G** (O.):

$$C_7H_7{\cdot}N_2{\cdot}C_7H_6{\cdot}N_2{\cdot}C_{10}H_6(SO_3H){\cdot}NH_2$$

Prepared by the action of diazotised aminoazotoluene on β-naphthylamine-6-sulphonic acid. The red aqueous solution gives with hydrochloric acid a dark reddish-brown precipitate. The solution in sulphuric acid is dark greenish-blue, and gives a brownish-red precipitate on dilution.

Bordeaux BX (By.):

$$C_8H_9{\cdot}N_2{\cdot}C_8H_8{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$

Prepared by the action of diazotised aminoazoxylene on β-naphthol-6-sulphonic acid. Solution in water is brownish-red, and gives a brownish-red precipitate with hydrochloric acid or sodium hydroxide. Sulphuric acid dissolves colour to a green solution, which gives a reddish-brown precipitate on dilution.

Literature.—E. P. 5003 of 1879; D. R. P. 16482.

Union Fast Claret (Lev.):

$$C_8H_9{\cdot}N_2{\cdot}C_8H_8{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH(\beta)$$

Prepared by the action of diazotised aminoazoxylene on β-naphthol-3 : 6-disulphonic acid. Soluble in water with a Bordeaux-red colour; reddish-brown flocculent precipitate on adding dilute acid. Solution in sulphuric acid dark blue, giving reddish-brown precipitate on dilution.

Literature.—E. P. 5003 and 5021 of 1879, 536 of 1880; D. R. P. 22010; A. P. 210233, 246221.

Croceïne Scarlet 3 B (By.) (K.) (T. M.); **Erythrine 2 R** (B.); **Ponceau 4 RB** (A.):

$$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$

Produced by the action of diazotised aminoazobenzenesulphonic acid on β-naphthol-8-sulphonic acid (Bayer's). Solution not precipitated by alkali; a red precipitate produced by barium chloride, becoming dark-violet and crystalline on boiling. Dissolves in sulphuric acid with a deep-blue colour, becoming violet and then red on dilution.

Literature.—E. P. 1225 and 2030 of 1881, 2411 of 1883, 8390 of 1884; D. R. P. 18027; F. P. 142024; A. P. 256380.

Fast Scarlet B (K.):

$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$

Prepared by the action of diazotised aminoazobenzenemonosulphonic acid on β-naphthol-6-sulphonic acid (Schaffer's). Red solution in water, giving brown precipitate with hydrochloric acid and a red-violet colouration with sodium hydroxide. Solution in sulphuric acid is blue, and becomes red on dilution.

Literature.—D. R. P. 16482.

Cloth Scarlet G (K.):

$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$

Prepared by the action of diazotised aminoazobenzenemonosulphonic acid on β-naphthol. The scarlet solution in water gives a brown precipitate with sodium hydroxide, and becomes yellower on addition of hydrochloric acid when dilute, but in concentrated solutions a light-red precipitate is produced. The solution in sulphuric acid is green, becoming red on dilution.

Literature.—E. P. 5003 and 5021 of 1879, 536 of 1880; D. R. P. 16482.

Milling Orange (D.):

$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH$

Prepared by the action of diazotised aminoazobenzenemonosulphonic acid on salicylic acid. Orange-red solution in water, giving greyish-yellow precipitate with hydrochloric acid, and a dark-red solution and precipitate with sodium hydroxide. The solution in sulphuric acid is violet, giving a greyish-yellow precipitate on dilution.

Ponceau 3 RB (A.) (B K.); **New Red L** (K.); **Ponceau B extra** (M.); **Fast Ponceau B** (B.); **Double Scarlet** (K.); **Scarlet EC** (C.); **Blackley Scarlet** (Lev.); **Scarlet B** (P.):

$HSO_3{\cdot}C_6H_4{\cdot}N_6{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$

Prepared from diazotised aminoazobenzenedisulphonic acid and β-naphthol. Solution not precipitated by alkali; a brown flocculent precipitate by dilute acids. Dissolves in sulphuric acid with a green colour, becoming first blue and finally brown and precipitating on dilution.

Literature.—E. P. 5003 of 1879, 529 of 1880; D. R. P. 16482; A. P. 224927, 224928; Nietzki, Ber. 1880, 13, 800, 1838; Miller, *ibid.* 542, 803, 980.

Croceïne Scarlet O extra (K.):

$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_{10}H_4(SO_3H){\cdot}OH$

Prepared by the action of diazotised aminoazobenzenedisulphonic acid on β-naphthol-8-sulphonic acid. The yellowish-red aqueous solution gives a violet colouration with hydrochloric acid or sodium hydroxide. The solution in sulphuric acid is blue, becoming yellowish-red on dilution.

Croceïne Scarlet 7 B (Ruch & Fils); **Ponceau 6 RB** (A.); **Croceine Scarlet 8 B** (K.) (By.); **Erythrine 7 B** (B.); **Cocceïne 7 B** (P.):

$HSO_3{\cdot}C_7H_6{\cdot}N_2{\cdot}C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH(\beta)$

Prepared by the action of diazotised aminoaz toluenesulphonic acid on β-naphthol-8-sulphoni acid (Bayer's) in presence of alkali. Resemble croceïne scarlet 3 B in general properties; give a crystalline magnesium salt on adding magnesium sulphate to hot concentrated solution an allowing to cool. Dissolves with a blue colou in sulphuric acid, becoming red on dilution.

Literature as for croceïne scarlet 3 B; an A. P. 256375.

Orseilline 2 B (By.). Prepared by the actio of diazotised aminoazotoluenesulphonic aci on α-naphthol-4-sulphonic acid. Dissolves wit a blue colour in sulphuric acid, becoming re on dilution.

Literature.—E. P. 2237 and 4237 of 1883 D. R. P. 26012.

Bordeaux G (By.) (M.). Prepared by th action of diazotised aminoazotoluenemon sulphonic acid on β-naphthol-6-sulphonic aci

Literature.—E. P. 5003 of 1879; D. R. 16482, 16483.

Eriochrome Verdone A (G.):

$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_7H_5(OH){\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$

Sulphanilic acid is diazotised and combined wit *m*-amino-*p*-cresol and the product is diazotise and combined with β-naphthol. The viole aqueous solution becomes claret-red wit hydrochloric acid, and blue-green with sodiu hydroxide. The solution in sulphuric acid i green, giving a brown-red precipitate on dilution. Wool is dyed in claret-red shades fro an acid-bath and on chroming becomes blue green.

Literature.—E. P. 13903 and 13904 of 1909 D. R. P. 201377, 224024, 227197; F. P. 40453

Ponceau 10 RB (A.):

$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(O{\cdot}CH_3){\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$

Sulphanilic acid is diazotised and combine with *o*-anisidine, and the product diazotise and combined with β-naphthol-8-sulphonic acid The aqueous solution is red, and that in sulphuric acid blue.

Janus Red B (M.):

$N(CH_3)_3Cl{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(CH_3){\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$

Prepared by diazotising *m*-aminophenyltrimethylammonium chloride, combining wit *m*-toluidine, diazotising the product and combining with β-naphthol. The red aqueou solution gives a brownish-red precipitate wit hydrochloric acid and a bluish-violet precipitat with sodium hydroxide. The solution in sulphuric acid is green, and gives a red precipitat on dilution.

Literature.—E. P. 5119 of 1897, 10596 o 1898; D. R. P. 93499, 95718, 98585, 100919 F. P. 264579; A. P. 623697.

Neutral Grey G (A.):

$C_6H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(NH_2){\cdot}OH$

Diazotised benzeneazo-α-naphthylamine is combined with 7-amino-α-naphthol-3-sulphonic aci (γ-acid). It gives a blackish-violet solution i water, and a bluish-green in sulphuric acid.

Literature.—D. R. P. appl. A. 3743.

Nyanza Black B (A.):

$NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(NH_2){\cdot}OH$

Prepared by the action of diazotised *p*-amino benzeneazo-α-naphthylamine (only one amino-group is diazotised)[1] on 7-amino-α-naphthol-3-sulphonic acid (γ-acid). Solution is dark-violet and gives violet precipitates with hydrochloric acid and sodium hydroxide. The solution in sulphuric acid is blue, and gives a violet precipitate on dilution. The colouring matter itself produces only indifferent shades, but when diazotised and developed on the fibre fast shades are obtained. When developed with *m*-tolylenediamine, a brown-black is obtained, and with β-naphthol a navy-blue.

Literature.—E. P. 277 and 6630 of 1892; D. R. P. 72393, 72394, 80421; F. P. 221378; A. P. 491410, 511688, 512167.

Coomassie Wool Black R (Lev.):

$$NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$

Prepared by the action of diazotised *p*-acetylaminobenzeneazo-α-naphthylamine on β-naphthol-6-sulphonic acid (Schaffer's), and hydrolysing the product. The dark-violet solution gives a precipitate with hydrochloric acid. The solution in sulphuric acid is green, becoming red on dilution.

Literature.—E. P. 24980 of 1899; D. R. P. 122457; A. P. 654167, 654168.

Coomassie Wool Black S (Lev.):

$$NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$$

Prepared as the preceding dyestuff, the final component being β-naphthol-3 : 6-disulphonic acid (R-salt). The blue-black aqueous solution becomes redder with hydrochloric acid. The solution in sulphuric acid is green, becoming red on dilution.

Literature.—as above.

Diaminogen BB extra (C.):

$$NH_2{\cdot}C_{10}H_5(SO_3H){\cdot}N_2\,C_{10}H_6\,N_2\,C_{10}H_5(SO_3H){\cdot}OH$$

Monoacetyl-1 : 4-naphthylenediamine-7-sulphonic acid is diazotised and combined with α-naphthylamine, the intermediate product diazotised and combined with 7-amino-α-naphthol-3-sulphonic acid (γ-acid), and the product hydrolysed. When diazotised and developed on the fibre a fast black is produced.

Literature.—E. P. 15444 of 1893; D. R. P. 78831, 79910; F. P. 232209; A. P. 533463, 560796.

Diaminogen Blue BB (C.); **Diazanil Blue BB** (M.). Prepared as the preceding, but the end component is β-naphthol-6-sulphonic acid (Schaffer's).

Literature as above.

Diaminogen Blue G (C.). Prepared as above, the end-component being β-naphthol-3 : 6-disulphonic acid (R-salt).

Literature as above.

Diazo Indigo Blue is an analogous product.

Zambesi Sky Blue 4 B (A.). Prepared from diazotised monoacetyl-3 : 6-diaminocresyl methyl ether combined with α-naphthylamine,[2] the intermediate product being diazotised and combined with β-naphthol-6-sulphonic acid and the end-product saponified. The reddish-violet aqueous solution becomes redder with hydrochloric acid and bluer with sodium hydroxide. The solution in sulphuric acid is blue, and becomes violet-red on dilution.

Literature.—E. P. 2188 of 1901; D. R. P. 126172.

Victoria Black B (By.):

$$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_4(OH)_2{\cdot}SO_3H$$

Prepared by the action of diazotised *p*-sulphobenzeneazo-α-naphthylamine on 1 : 8-dihydroxynaphthalene-4-sulphonic acid. The dark reddish-violet aqueous solution gives with hydrochloric acid a Bordeaux-red precipitate, and with sodium hydroxide becomes dark-blue violet. The solution in sulphuric acid is moss-green, changing on dilution to sea-green, and then to bluish-red.

Literature.—E. P. 13665 of 1889; D. R. P. 61707, 62945; F. P. 200520; A. P. 466202.

Buffalo Black 10 B (Sch.); **Acid Black N** (P.):

$$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2$$

Prepared as the preceding, except that 1 : 8-aminonaphthol-3 : 6-disulphonic acid (H-acid) is used as the end-component. The solutions in water or sulphuric acid are blue.

Literature.—A. P. 618963.

Jet Black R (By.):

$$(HSO_3)_2C_6H_3{\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_6H_5$$

Prepared by the action of diazotised disulphobenzeneazo-α-naphthylamine on phenyl-α-naphthylamine. The bluish-violet aqueous solution gives a bluish-black precipitate with hydrochloric acid, and a soluble violet precipitate with sodium hydroxide. Sulphuric acid dissolves the colouring matter to a blue solution, which gives a greenish-blue precipitate on dilution.

Literature.—E. P. 14442 of 1888; D. R. P. 48924; F. P. 193430; A. P. 425885.

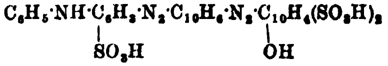
Diamond Black F (By.) (B.) (L.); **Chrome Fast Black FRW** (I.); **Chrome Deep Black** (T. M.); **Salicin Black D** (K.); **Era Black F** (Lev.); **Fast Chrome Black B** (Sch.); **Fast Mordant Black B, T** (M.); **Chrome Black J** (H.):

$$CO_2H{\cdot}C_6H_3(OH){\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$

Aminosalicylic acid is diazotised and combined with α-naphthylamine, and the product diazotised and combined with α-naphthol-4- (or 5-) sulphonic acid. Bluish-violet solution gives violet precipitate with hydrochloric acid, and becomes blue with sodium hydroxide. Solution in sulphuric acid is greenish, giving a violet precipitate on dilution. Similar dyestuffs are **Era Blacks J** and **NG** (Lev.).

Literature.—E. P. 8209 of 1889; D. R. P. 51504; F. P. 198521; A. P. 438438.

Nerol B (A.):



$$\underset{\textstyle SO_3H}{C_6H_5{\cdot}NH{\cdot}C_6H_3}{\cdot}N_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}\underset{\textstyle OH}{C_{10}H_4}(SO_3H)_2$$

p-Aminodiphenylamine-*o*-sulphonic acid is diazotised and combined with α-naphthylamine, and the intermediate product is diazotised and combined with β-naphthol-3 : 6-disulphonic acid (R-salt). Dark violet-blue solution in water gives a blue precipitate with hydrochloric acid. The solution in sulphuric acid is dark blue-violet, giving a blue-violet precipitate on dilution.

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[1] All the authorities give the above constitution for this colouring matter, but it is generally understood that a benzenoid amino- group is diazotised preferably to a naphthalenoid amino- group.

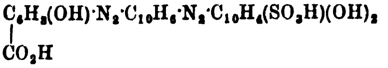
[2] According to Buntrock (Zeitsch. Farben-Ind. 1902, 1, 224). The patents quoted give the 6- or 7-sulphonic acid as intermediate component.

Literature.—E. P. 24527 of 1897; D. R. P. 101274; F. P. 271609.

Nerol 2 B (A.). Prepared as the preceding, except that the last component is α-naphthol-4-sulphonic acid.

Properties and literature as above.

Diamond Green (By.):



$$\underset{\displaystyle CO_2H}{\underset{|}{C_6H_3}}(OH)\cdot N_2\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)_2$$

Prepared by diazotising aminosalicylic acid and combining with α-naphthylamine, the intermediate product being diazotised and combined with 1 : 8-dihydroxynaphthalene-4-sulphonic acid. The blackish-violet aqueous solution gives a dark reddish-violet precipitate with hydrochloric acid, and becomes dark blue with sodium hydroxide. The solution in sulphuric acid is bluish-green, becoming greenish-blue, and finally giving a blackish-violet precipitate on dilution.

Literature.—E. P. 8299 of 1889 1828 of 1890; D. R. P. 51504, 62003; F. P. 198521; A. P. 438438.

Naphthylamine Black D (C.) (K.); **Deep Black D, conc.** (T. M.); **Coomassie Wool Black D** (Lev.); **Buffalo Black AD** (Sch.); **Acid Black NN** (I.); **Naphthalene Black R** (H.):

$$(HSO_3)_2C_{10}H_5\cdot N_2\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_6\cdot NH_2$$

α-Naphthylamine-3 : 6-disulphonic acid is diazotised and combined with α-naphthylamine, and the intermediate product diazotised and combined with α-naphthylamine. The violet-black aqueous solution gives a black precipitate with hydrochloric acid. The solution in sulphuric acid is bluish-black, and on dilution becomes green, and finally gives a black precipitate.

Literature.—E. P. 18425 of 1888; D. R. P. 50907; F. P. 170342; A. P. 412440.

Naphthylamine Black 4 B (C.); **Naphthalene Black D** (H.) is a mixture of Naphthol blue-black and the preceding colouring matter.

Naphthyl Blue Black N (C.); **Alphyl Blue Black O** (M.). 4 : 7-Disulphonaphthaleneazo-α-naphthylamine is diazotised and combined with aminonaphthol ethyl ether. The dark-violet aqueous solution turns blue and gives a blackish-blue precipitate with hydrochloric acid, and becomes blue and precipitates with sodium hydroxide. The solution in sulphuric acid is dark blue, which on dilution becomes blue, and finally bluish-violet.

Literature.—Chem. Ind. 1896, 19, 548.

Anthracite Black B (C.); **Phenylene Black** (P.):

$$(HSO_3)_2C_{10}H_5\cdot N_2\cdot C_{10}H_6\cdot N_2\cdot C_6H_3(NH\cdot C_6H_5)_2$$

α-Naphthylamine-3 : 6-(4 : 7-in the case of the latter dye) -disulphonic acid is diazotised and combined with α-naphthylamine, and the product diazotised and combined with diphenyl-*m*-phenylenediamine. The dull-violet aqueous solution gives a violet precipitate with hydrochloric acid. The solution in sulphuric acid is black, giving a greenish-black precipitate on dilution.

Literature.—E. P. 4825 and 7977 of 1889; D. R. P. 52616, 61202; F. P. 196793, 197963; A. P. 502912.

Naphthol Black B (C.); **Brilliant Black B** (B.); **Naphthol Black OPAS** (Lev.); **Buffalo Black 2 B** (Sch.); **Carbon Black B, 3 B** (M.); **Wool Black B, SG** (D.):

$$(HSO_3)_2C_{10}H_5\cdot N_2\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_4(SO_3H)_2.OH$$

β-Naphthylamine-6 : 8-disulphonic acid is diazotised and combined with α-naphthylamine, and the product diazotised and combined with β-naphthol-3 : 6-disulphonic acid (R-salt). The violet aqueous solution gives with hydrochloric acid a reddish-violet and with sodium hydroxide a blue precipitate. The solution in sulphuric acid is green, becoming bluer on dilution, and then giving a reddish-violet precipitate.

Literature.—E. P. 9214 of 1885; D. R. P. 39029; F. P. 170342; A. P. 345901.

Naphthol Black 2 B (Lev.) is prepared as the preceding, but starting with α-naphthylamine-3 : 6-disulphonic acid.

Naphthol Black 6 B (C.) (K.); **Acid Black 6 B** (H.); **Brilliant Black BD** (B.); **Naphthalene Black 5 B** (P.); **Naphthol Black** (D.); **Acid Black 5 B, BR** (T. M.); **Wool Black** (B. K.); **Acidol Black** (T. M.) is prepared by the action of diazotised 4 : 7-disulphonaphthaleneazo-α-naphthylamine on β-naphtholdisulphonic acid (R-salt). Aqueous solution dark violet, becoming dark blue with acid or alkali; dissolves in sulphuric acid with a dark-green colour, becoming blue on dilution.

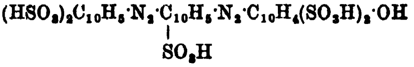
Literature.—E. P. 9214 of 1885; D. R. P. 39029; F. P. 170342; A. P. 345901.

Sulphone Black G, R (By.):

$$C_6H_5\cdot N_2\cdot C_{10}H_5(SO_3H)\ N_2\cdot C_{10}H_4(OH)_2\cdot SO_3H$$

Diazotised aniline is combined with α-naphthylamine-6-(or 7)-sulphonic acid, the product diazotised and combined with 1 : 8-dihydroxynaphthalene-4-sulphonic acid. The aqueous solution is reddish-violet, and that in sulphuric acid is greenish-blue.

Biebrich Patent Black BO (K.):



$$(HSO_3)_2C_{10}H_5\cdot N_2\cdot \underset{\displaystyle SO_3H}{\underset{|}{C_{10}H_5}}\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH$$

α-Naphthylaminedisulphonic acid is diazotised and combined with α-naphthylamine-6-(or 7)-sulphonic acid, the product diazotised and combined with β-naphthol-3 : 6-disulphonic acid (R-salt). The dark reddish-violet aqueous solution is turned slightly blue with hydrochloric acid and pure blue with sodium hydroxide. Solution in sulphuric acid is dark greenish-blue, becoming dark violet on dilution.

Literature.—E. P. 2718 of 1892; D. R. P. 73901, 83572, 84460; F. P. 219424; A. P. 476070, 546068, 546069.

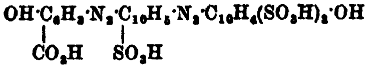
Biebrich Patent Black 4 AN (K.):

$$HSO_3\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot N_2\cdot C_{10}H_6\cdot NH_2$$

Prepared from diazotised naphthionic acid and α-naphthylamine-6-(or 7)-sulphonic acid, the product being diazotised and combined with α-naphthylamine. The violet aqueous solution gives a bluish-black precipitate with hydrochloric acid, and becomes blue with sodium hydroxide. Solution in sulphuric acid is bluish-green, giving a bluish-black precipitate on dilution. Similar dyestuffs bear the brands 6 AN, 4 BN, and 6 BN.

References as above.

Anthracene Acid Black (various marks) (C.):



$$\mathrm{OH{\cdot}}\underset{\substack{|\\ CO_2H}}{C_6H_3}{\cdot}N_2{\cdot}\underset{\substack{|\\ SO_3H}}{C_{10}H_5}{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$$

Aminosalicylic acid is diazotised and combined with *a*-naphthylamine-6-(or 7)-sulphonic acid, and the product diazotised and combined with *β*-naphthol-3 : 6-disulphonic acid (R-salt). The violet aqueous solution gives a violet precipitate with hydrochloric acid, and becomes bluish-violet with sodium hydroxide. Solution in sulphuric acid is green, giving a violet precipitate on dilution.

Naphthalene Acid Black 4 B (By.):

$$HSO_3{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2$$

Metanilic acid is diazotised and combined with the same acid as in the preceding, and the product diazotised and combined with *a*-naphthylamine. Aqueous solution is violet, becoming blue with hydrochloric acid, and redder with sodium hydroxide. Solution in sulphuric acid is blue, becoming violet on dilution.

Sulphocyanines (various marks) (By.); **Tolyl Blue GR extra, 5 R extra** (M.); **Coomassie Navy Blue** (various marks) (Lev.) are prepared from diazotised metanilic acid, which is combined with *a*-naphthylamine, the product being diazotised and combined with phenyl- or tolyl-*a*-naphthylamine-8-sulphonic acid. The violet aqueous solution gives a greyish-blue precipitate with hydrochloric acid. Solution in sulphuric acid is blue, becoming greener and giving a blue precipitate on dilution. Similar dyes are **Sulphone Black 3 B, 4 BT** (By.) (*cf.* D. R. P. 75571).

Literature.—D. R. P. 118655.

Sulphoncyamine Black B, 2 B (By.); **Tolyl Black B, BB** (M.). *a*-Naphthylamine-5-sulphonic acid is diazotised and combined with *a*-naphthylamine (or with Cleve's acids), the product being diazotised and combined with phenyl-*a*-naphthylamine-8-sulphonic acid. The aqueous solution is violet, and that in sulphuric acid dark blue.

Literature.—D. R. P. 118655.

Brilliant Croceine 9 B (C.):

$$(HSO_3)_2C_{10}H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH$$

β-Naphthylamine-6 : 8-disulphonic acid is diazotised and combined with aniline, the product being diazotised and combined with a mixture of *β*-naphthol-3 : 6- and 6 : 8-disulphonic acids. The bluish-red aqueous solution becomes darker and bluer with hydrochloric acid, and brownish with sodium hydroxide. The solution in sulphuric acid is blue, changing to bluish-red on dilution.

Fast Sulphone Black F, FB (K. S.):

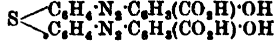
$$HSO_3{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$$

Naphthionic acid is diazotised and combined with 1 : 8-aminonaphthol-3 : 6-disulphonic acid (H-acid), the product diazotised and combined with *β*-naphthol. The solution in water is greenish-black, and in sulphuric acid blackish-violet.

Literature.—E. P. 14768 of 1903; D. R. P. 158134.

C. Tetrazo- Colouring Matters.

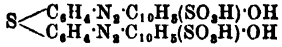
Anthracene Yellow C (C.) (By.); **Fast Mordant Yellow GI** (B.); **Acid Alizarine Yellow RC** (M.):



$$S\left\langle\begin{array}{l}C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH\\ C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH\end{array}\right.$$

Prepared from tetrazotised thioaniline and salicylic acid (2 mols.). The light yellowish-brown aqueous solution gives a greenish-brown precipitate with hydrochloric acid. The solution in sulphuric acid is dark reddish-violet, giving a yellowish-grey precipitate on dilution.

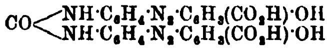
Milling Red G (C.):



$$S\left\langle\begin{array}{l}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH\\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH\end{array}\right.$$

Similarly prepared from tetrazotised thioaniline and *β*-naphthol-6-sulphonic acid (Schäffer's). The orange-red aqueous solution gives a brown precipitate with hydrochloric acid. The solution in sulphuric acid is reddish-violet, giving a brown precipitate on dilution.

Cotton Yellow G (B.); **Benzo Fast Yellow 5 GL** (By.); **Diamine Fast Yellow 3 G** (C.):

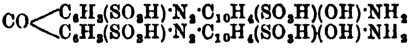


$$CO\left\langle\begin{array}{l}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH\\ NH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH\end{array}\right.$$

p-Aminoacetanilide is diazotised and combined with salicylic acid, the product hydrolysed and treated with carbonyl chloride. The yellow aqueous solution gives a brown precipitate with hydrochloric acid, and becomes rather more orange with sodium hydroxide. The solution in sulphuric acid is orange-red, giving a bluish-violet precipitate on dilution.

Literature.—E. P. 15258 of 1888; D. R. P. 46737, 47902; A. P. 430535.

Benzo Fast Pink 2 BL (By.):

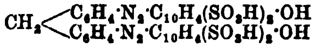


$$CO\left\langle\begin{array}{l}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2\\ C_6H_3(SO_3H){\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2\end{array}\right.$$

Prepared from tetrazotised di-*p*-aminodiphenylcarbamidedisulphonic acid and 7-amino-*a*-naphthol-3-sulphonic acid (*γ*-acid; 2 mols.) in neutral or acid solution. The red aqueous solution becomes reddish-violet with hydrochloric acid and yellower with sodium hydroxide. The solution in sulphuric acid is blue, giving an almost black precipitate on dilution.

Literature.—E. P. 11766 of 1901; D. R. P. 129388, 131513; F. P. 311339; A. P. 687171; Zeitsch. Farben.-Ind. 1902, 1, 192; Chem. Zeit. 1902, 26, 485.

Milling Red R (D.):



$$CH_2\left\langle\begin{array}{l}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH\\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH\end{array}\right.$$

Prepared from tetrazotised diaminodiphenylmethane and *β*-naphthol-3 : 6-disulphonic acid (R-salt; 2 mols.). The corresponding colour from diaminodixylylmethane is **Cinnabar Scarlet BF** (B. K.), and that from diaminodixylylphenylmethane is **Cotton Ponceau** (B. K.); **Cinnabar Scarlet G, R** (B. K.). They are all also used for the preparation of lakes.

Literature.—D. R. P. 43644.

Bismarck Brown (most firms); **Manchester Brown**; **Phenylene Brown**; **Vesuvine**; **Leather Brown**; **Cinnamon Brown**; **English Brown**; **Brown A** (P.):

$$(NH_2)_2C_6H_3{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(NH_2)_2$$

Prepared by adding a solution of 42·5 kilos of sodium nitrite and 127·5 kilos of hydrochloric acid to a solution of *m*-phenylenediamine prepared by reducing 250 kilos of *m*-dinitrobenzene. The commercial product is the hydrochloride. The aqueous solution gives a brown precipitate with sodium hydroxide. The solution in sulphuric acid is brown, becoming red on dilution.

Literature.—E. P. 3307 of 1863; Zeitsch. f. Chem. 1867, 3, 278; Ber. 1897, 30, 2111, 2203, 2899.

Azo Alizarine Bordeaux W (D. H.):

$$CO_2H{\cdot}C_6H_3(OH){\cdot}N_2\,C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$

p-Aminoacetanilide is diazotised and combined with salicylic acid, the product hydrolysed and diazotised and combined with *a*-naphthol-4-sulphonic acid. The aqueous solution is red, and that in sulphuric acid is blue.

Literature.—E. P. 1033 of 1899; D R. P. appl. D 9290; F. P. 284775; A. P. 631089.

Azo Alizarine Black I (D. H.). Prepared as the preceding, except that the end-component is 1 : 8 dihydroxynaphthalene-3 : 6-di (or 4-mono)-sulphonic acid The aqueous solution is violet, and that in sulphuric acid blue.

Literature.—E P. 1033 of 1899; D R. P. appl. D. 9290; F. P. 284775; A. P. 640010, 628721.

Violet Black (B.):

$$NH_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH$$

p-Aminoacetanilide is diazotised and combined with 1 mol. of *a*-naphthol 4-sulphonic acid. The acetyl- group is then removed by heating with alkali, and the amino- compound is diazotised and combined with 1 mol. of *a*-naphthylamine. Aqueous solution brownish-red, giving violet precipitate with mineral acids and reddish-violet colouration with acetic acid or with sodium hydroxide; blue solution in sulphuric acid giving violet precipitate on dilution.

Literature.—D. R P. 42814.

Ingrain Black C (*H.*):

$$HSO_3\,C_{10}H_5(NH_2){\cdot}N_2{\cdot}C_6H_4\,C_{10}H_4(SO_3H)(OH)\,NH_2$$

p-Aminoacetanilide is diazotised and combined with *a*-naphthylamine-6 (or 7)-sulphonic acid (Cleve's acid), the product hydrolysed, diazotised, and combined with 1 mol of 7-amino-*a*-naphthol-3-sulphonic acid (γ-acid).

Acid Alizarine Black SE (M.); **Palatine Chrome Black F** (B.):

$$HSO_3{\cdot}C_6H_2(OH)(N_2\,C_{10}H_6{\cdot}OH)_2$$

Prepared from tetrazotised 2 : 6-diaminophenol-4-sulphonic acid and *β*-naphthol (2 mols.). Dark-blue aqueous solution gives a red precipitate with hydrochloric acid and a greenish-blue precipitate with sodium hydroxide. The solution in sulphuric acid is violet, giving a red precipitate on dilution.

Literature.—E. P. 18624 of 1900, 16811 and 2397 of 1901; D. R. P. 147880, 150373; F. P. 304694, 308588, 310597, 313671; A. P. 665696, 677231.

Acid Alizarine Black SN (M.); **Palatine Chrome Black S** (B.). Similar to the above, except that 1 mol. of *β*-naphthol and 1 mol. of *β*-naphthol-6-sulphonic acid are used as components. The blue aqueous solution gives a red precipitate with hydrochloric acid, and becomes violet with sodium hydroxide. The solution in sulphuric acid is violet, giving a reddish-brown precipitate on dilution.

Literature.—E. P. 2397 and 16811 of 1901; *D. R. P. 148212, 150373; F. P. 308000, 310597,* 313671; A. P. 680283, 677227.

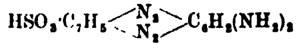
Manchester Brown EE (C.) (Lev.); **Bismarck Brown R** (I.) (By.) (O.) (H.) (Central Dyestuff and Chemical Co.) (Ault and Wiborg Co.), &c.; **Bismarck Brown 2 R. conc.** (T. M.); **Bismarck Brown T** (D. H.); **Vesuvine B** (B.); **Brown N** (P.); **Buffalo Brown 53** (Sch.):

$$(NH_2)_2C_7H_5{\cdot}N_2{\cdot}C_7H_6{\cdot}N_2{\cdot}C_7H_5(NH_2)_2$$

Prepared in the same manner as Bismarck brown, but *m*-tolylenediamine is used instead of *m*-phenylenediamine. The reddish-brown aqueous solution becomes yellowish-brown with hydrochloric acid, and gives a light-brown precipitate with sodium hydroxide. The solution in sulphuric acid is dark brown, becoming first red and then brown on dilution.

Literature.—Griess, Ber. 1878, 11, 627.

Toluylene Brown G (O.) (By.):



$$HSO_3{\cdot}C_7H_5\begin{smallmatrix}\diagup N_2 \diagdown\\ \diagdown N_2 \diagup\end{smallmatrix}C_6H_2(NH_2)_2$$

Prepared by the action of tetrazotised tolylenediaminesulphonic acid ($CH_3 \cdot NH_2 : SO_3H : NH_2$ = 1 : 2 : 4 : 6) on 1 mol. of *m*-phenylenediamine. Solution in water is brown, and in sulphuric *acid brownish-red.*

Literature.—E P. 17546 of 1892; D. R. P. 65853; A. P. 516380.

Toluylene Yellow (O.). Prepared from the same tetrazo-compound as the preceding, and 2 mols. of 6-nitro-*m*-phenylenediamine in hydrochloric acid solution. The yellowish-brown aqueous solution gives brown precipitates with hydrochloric acid and sodium hydroxide. The solution in sulphuric acid is brown.

Literature.—E. P. 1331 of 1896; D. R. P. 86940; A. P. 568549.

Toluylene Orange RR (O.). Prepared from the same tetrazo-compound as before, and 2 mols. of *β*-naphthylamine. The yellowish-red aqueous solution gives a brownish-red precipitate with hydrochloric acid, and a yellowish-red precipitate with sodium hydroxide. The solution in sulphuric acid is bluish-grey.

Literature.—E. P. 17546 of 1892; D. R. P. 70147; A. P. 497032.

Diamine Gold Yellow (C.):

$$C_2H_5{\cdot}O{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}N_2{\cdot}C_6H_4{\cdot}O{\cdot}C_2H_5$$

Prepared from tetrazotised 1 : 5-naphthylenediamine-3 : 7-disulphonic acid and phenol (2 mols.), the product then being ethylated. The yellow aqueous solution gives a brownish-yellow precipitate with hydrochloric acid and a yellow precipitate with sodium hydroxide. The solution in sulphuric acid is reddish-violet, becoming green and then yellow on dilution.

Literature.—E. P. 15346 of 1890; D. R. P. 61174; F. P. 182063, 208526; A. P. 472121.

Naphthylene Violet (C.):

$$NH_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2$$

Prepared from the preceding tetrazo- compound and *a*-naphthylamine (2 mols.). The Bordeaux-red aqueous solution gives a blue precipitate with hydrochloric acid, and a red precipitate with sodium hydroxide. The solution in sulphuric acid is blue, and gives a violet precipitate on dilution. The colouring matter is usually diazotised and developed on the fibre or treated on the fibre with nitrous acid, the latter colour being known as **Diamine Cutch**, which is a fast brown shade.

Literature.—E. P. 15346 and 15347 of 1890; D. R. P. 62075; F. P. 208526, 208570; A. P. 464566.

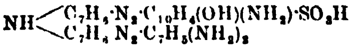
Coomassie Navy Blue (Lev.):

$$(HSO_3)_2C_{10}H_4(OH)\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot N_2\cdot C_{10}H_6\cdot OH$$

Prepared by diazotising 1 : 4-naphthylenediamine-2-sulphonic acid (only one amino-group can be diazotised), combining with β-naphthol-3 : 6-disulphonic acid, diazotising the product (the second amino- group can now be diazotised), and combining with β-naphthol. Dark-blue aqueous solution becomes violet with sodium hydroxide. Solution in sulphuric acid is blue-green, becoming dark blue on dilution.

Literature.—E. P. 2946 of 1896; D. R. P. 102160; F. P. 256862; A. P. 619194, 634009, 639748.

Diphenyl Fast Black[1] (G.):

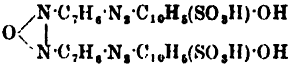


$$NH\left<\begin{array}{l}C_7H_6\cdot N_2\cdot C_{10}H_4(OH)(NH_2)\cdot SO_3H\\ C_7H_6\cdot N_2\cdot C_7H_5(NH_2)_2\end{array}\right.$$

Prepared from tetrazotised *p*-diaminoditolylamine and 1 mol. of 7-*amino*-α-naphthol-3-sulphonic acid (γ-acid) and 1 mol. of *m*-tolylenediamine. The violet-black aqueous solution gives with hydrochloric acid a bluish-black precipitate, and with sodium hydroxide a black precipitate. The solution in sulphuric acid is dark blue, and gives a black precipitate on dilution.

Literature.—E. P. 16582 of 1896; F. P. 258521; A. P. 575904.

Dianthine (Claus & Co); **St. Denis Red** (P.); **Rosophenine 4 B** (Cl. Co.); **Rosanol 4 B** (K.); **Cotton Red S** (B.):

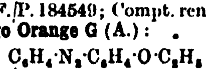


$$O\left<\begin{array}{l}N\cdot C_7H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH\\ \vert\\ N\cdot C_7H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH\end{array}\right.$$

Prepared from tetrazotised diaminoazoxytoluene and α-naphthol-4-sulphonic acid (2 mols) The red aqueous solution gives red precipitates with hydrochloric acid and sodium hydroxide. The solution in sulphuric acid is red, and gives a red precipitate on dilution

Literature.—E. P. 9315 and 11976 of 1887, 5736 of 1890, 19891 of 1892; D. R. P. 44045, 44554; F. P. 184549; Compt. rend. 1901, 132, 985

Congo Orange G (A.):

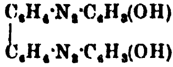


$$\begin{array}{l}C_6H_4\cdot N_2\cdot C_6H_4\cdot O\cdot C_2H_5\\ \vert\\ C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot NH_2\end{array}$$

Prepared from tetrazotised benzidine[2] and 1 mol. of β-naphthylamine-3 : 6-disulphonic acid, and 1 mol. of phenol, the product being ethylated. The orange-yellow aqueous solution gives a brown precipitate with hydrochloric acid. The solution in sulphuric acid is blue, becoming reddish-violet on dilution, and finally giving a brown precipitate. The corresponding colouring matter from tolidine is **Congo Orange R** (A.).

Literature.—E. P. 17957 of 1889; D. R. P. 52328; F. P. 160722.

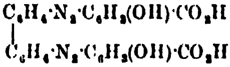
Pyramidol Brown BG (Farbwerk Ammersfoort):



$$\begin{array}{l}C_6H_4\cdot N_2\cdot C_6H_3(OH)_2\\ \vert\\ C_6H_4\cdot N_2\cdot C_6H_3(OH)_2\end{array}$$

Prepared from tetrazotised benzidine and resorcinol (2 mols.). The orange-brown aqueous solution gives a brown precipitate with hydrochloric acid, and becomes Bordeaux-red with sodium hydroxide. The solution in sulphuric acid is reddish-violet, giving a brown precipitate on dilution. Cotton dyed red with this colouring matter is converted into a deep brown when treated with a diazo- compound on the fibre.

Chrysamine G (By.) (A) (Lev.) (H.) (L.) (T. M.) (K. S.) (Barking Chemicals Co.) (Marden, Orth, and Hastings Corporation) (Calco Chemical Co.); **Azidine Yellow G** (C. J); **Direct Yellow CG** (Sch.):

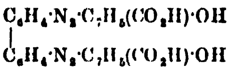


$$\begin{array}{l}C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H\\ \vert\\ C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H\end{array}$$

Prepared by the action of tetrazotised benzidine on salicylic acid (2 mols) in alkaline solution. Used for dyeing cotton goods yellow directly from a soap-bath. Aqueous solution orange, becoming redder on addition of sodium hydroxide; orange flocculent precipitate, with dilute sulphuric acid. Soluble in sulphuric acid, with a magenta-red colour, becoming orange and precipitating on dilution. The homologue from tetrazoditolyl is **Chrysamine R** (By.) (A.) (L) (Lev) (T M.) (K. S.).

Literature.—E. P. 9162 and 9606 of 1884; D. R. P. 31658; A. P. 329638.

Cresotine Yellow G (M) (O.):

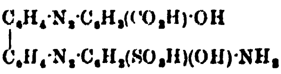


$$\begin{array}{l}C_6H_4\cdot N_2\cdot C_7H_5(CO_2H)\cdot OH\\ \vert\\ C_6H_4\cdot N_2\cdot C_7H_5(CO_2H)\cdot OH\end{array}$$

Prepared from tetrazotised benzidine and hydroxytoluic acid ($OH : CH_3 : CO_2H = 1 : 2 : 6$). Yellow aqueous solution gives a brownish-yellow precipitate with hydrochloric acid and becomes yellowish-red with sodium hydroxide. Solution in sulphuric acid is reddish-violet, precipitating on dilution. The corresponding colouring matter from tolidine is **Cresotine Yellow R** (O.); **Azidine Yellow R** (C. J.).

Literature.—E. P. 7097 of 1888; A. P. 394841.

Brilliant Orange G (A.) (By.):

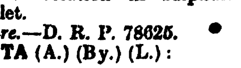


$$\begin{array}{l}C_6H_4\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH\\ \vert\\ C_6H_4\cdot N_2\cdot C_6H_2(SO_3H)(OH)\cdot NH_2\end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of salicylic acid and aminophenolsulphonic acid III. Yellowish-brown aqueous solution gives a violet-brown precipitate with hydrochloric acid. Solution in sulphuric acid is reddish-violet.

Literature.—D. R. P. 78625.

Orange TA (A.) (By.) (L.):



$$\begin{array}{l}C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2\\ \vert\\ C_6H_4\cdot N_2\cdot C_7H_7\cdot OH\end{array}$$

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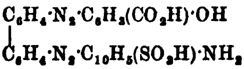
[1] **Diamine Deep Black** (C.) is derived from *p*-diaminodiphenylamine; **Pluto Black** (By.) also belongs to the same class.

[2] Benzidine or *p*-diaminodiphenyl is prepared by reducing nitrobenzene with zinc-dust and alkali to hydrazobenzene and converting this by means of acids into benzidine. The homologues of benzidine are prepared in a similar manner.

Prepared from tetrazotised benzidine and 1 mol. each of naphthionic acid and cresol. Reddish-brown aqueous solution gives a violet-blue precipitate with hydrochloric acid, and becomes redder with sodium hydroxide. Solution in sulphuric acid is blue, giving a blue precipitate on dilution.

Benzo Orange R (By.) (K. S.) (Marden, Orth, and Hastings Corporation):

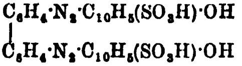


$$\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of salicylic acid and naphthionic acid. The orange-yellow aqueous solution becomes reddish-violet with hydrochloric acid, and gives a reddish-yellow precipitate with sodium hydroxide. Solution in sulphuric acid is violet-blue, giving a greyish-violet precipitate on dilution.

Literature.—E. P. 2213 of 1886; D. R. P. 44797; A. P. 447303.

Bordeaux COV (A.); **Bordeaux extra** (By.); **Bordeaux BL extra** (T. M.); **Azidine Violet R** (C. J.); **New Bordeaux L** (B.):

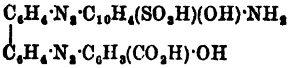


$$\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH \end{array}$$

Prepared from tetrazotised benzidine and β-naphthol-8-sulphonic acid (2 mols.). Bordeaux-red solution in water, and violet in sulphuric acid.

Literature.—E. P. 8495 of 1884; D. R. P. 30077.

Diamine Fast Red F (C.); **Dianol Fast Red F** (Lev.); **Azidine Fast Red F** (C. J.); **Oxamine Fast Red F** (B.); **Naphthamine Red H** (K.); **Dianil Fast Red PH** (M.); **Benzo Fast Red FC** (By.); **Columbia Fast Red F** (A.); **Triazol Fast Red C** (O.); **Diphenyl Fast Red** (G.); **Hessian Fast Red F** (L.); **Benzamine Fast Red F** (D.); **Direct Fast Red F** (Sch.) (I.):

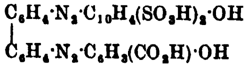


$$\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2 \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. of 7-amino-α-naphthol-3-sulphonic acid (γ-acid) combined in acid solution, and 1 mol. of salicylic acid. Red aqueous solution gives a brown precipitate with hydrochloric acid. The solution in sulphuric acid is reddish-blue, and gives a brown precipitate on dilution.

Literature.—E. P. 16699 of 1889; D. R. P. 57857; F. P. 201770.

Crumpsall Direct Fast Red R (Lev.):

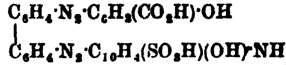


$$\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of β-naphthol-3 : 6-disulphonic acid (R-salt) and salicylic acid.

Literature.—E. P. 2213 of 1886; D. R. P. 44797; A. P. 447303.

Diamine Brown M (C.); **Chlorazol Brown M** (H.); **Renol Brown MB, conc.** (T. M.); **Azidine Brown M** (C. J.); **Naphthamine Brown H** (K.); **Crumpsall Direct Fast Brown B** (Lev.); **Dianil Brown MH** (M.); **Benzamine Brown M** (D.); **Direct Dark Brown M** (L.); **Direct Brown M** (I.); **Direct Brown 3 RB** (Sch.); **Oxamine Brown R** (B.):

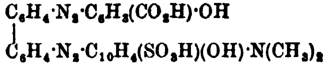


$$\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2 \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of salicylic acid and 7-amino-α-naphthol-3-sulphonic acid (γ-acid); the latter being combined in alkaline solution. The reddish-brown aqueous solution gives a brown precipitate with hydrochloric acid and a reddish-brown precipitate with sodium hydroxide. The solution in sulphuric acid is violet, changing to brown on dilution.

Literature.—D. R. P. 57857; F. P. 201770.

Diphenyl Brown BN (G.):

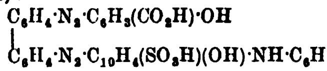


$$\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}N(CH_3)_2 \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of salicylic acid and 7-dimethylamino-α-naphthol-3-sulphonic acid. [The corresponding colouring matter from the monomethylamino-compound is **Diphenyl Brown RN** (G.).] The dark-brown solution gives a red precipitate with hydrochloric acid. The solution in sulphuric acid is bluish-violet, giving a red precipitate on dilution. When tolidine is used instead of benzidine, **Diphenyl Brown 3 GN** (G.) is obtained.

Literature.—E. P. 2771 of 1896; D. R. P. 103149; F. P. 250697; A. P. 567413.

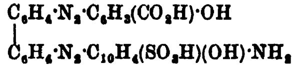
Diamine Brown B (C.); **Crumpsall Brown M** (Lev.):



$$\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH{\cdot}C_6H_5 \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of salicylic acid and 7-phenylamino-α-naphthol-3-sulphonic acid. The dark-brown aqueous solution gives a Bordeaux-red precipitate with hydrochloric acid, and becomes redder with sodium hydroxide. The solution in sulphuric acid is violet, giving a brown precipitate on dilution.

Oxamine Maroon (B.):



$$\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2 \end{array}$$

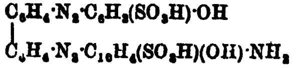
Prepared by combining tetrazotised benzidine with 1 mol. of 5-amino-α-naphthol-3-sulphonic acid in alkaline solution, and adding 1 mol. of salicylic acid to the product. The ruby-red aqueous solution does not change with acids or alkalis. The solution in sulphuric acid is dark violet, changing to wine-red on dilution.

Literature.—E. P. 2370 of 1893; D. R. P. 82572; F. P. 229263; A. P. 558344.

Oxamine Red (B.). Isomeric with the preceding. 6-Amino-α-naphthol-3-sulphonic acid is used instead of the 5-amino- acid. The red aqueous solution is not changed by hydrochloric acid, but becomes slightly more violet with sodium hydroxide. The solution in sulphuric acid is blue, changing to wine-red on dilution.

Literature.—E. P. 2614 of 1893; D. R. P. 93276; F. P. 227892; A. P. 555359.

Wool Red G (B.):



$$\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_6H_3(SO_3H){\cdot}OH \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2 \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of phenol-*o*-sulphonic acid and 7-amino-*α*-naphthol-3-sulphonic acid (γ-acid), the latter being combined in acid solution. The red aqueous solution gives a brown precipitate with hydrochloric acid, and becomes dark-red with sodium hydroxide. Solution in sulphuric acid is violet, giving a brown precipitate on dilution.

Literature.—D. R. P. appl. B. 29649 of 1901; F. P. 313533.

Diamine Scarlet B (C.); **Dianil Ponceau G** (M.)[1]:

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_6H_4\cdot O\cdot C_2H_5 \\ | \\ C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot NH_2 \end{array}$$

Tetrazotised benzidine is combined first with 1 mol. of *β*-naphthylamine-6 : 8-disulphonic acid, then with 1 mol. of phenol and the product is ethylated. The red aqueous solution becomes brownish-red with hydrochloric acid. The solution in sulphuric acid is violet, becoming brown on dilution.

Literature.—E. P. 12560 of 1889; D. R. P. 54084; F. P. 200152; A. P. 426345.

Pyramine Orange 2 R (B.):

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot NH_2 \\ | \\ C_6H_4\cdot N_2\cdot C_6H_2(NH_2)_2\cdot NO_2 \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of *β*-naphthylamine-3 : disulphonic acid and *p*-nitro-*m*-phenylenediamine. The yellow aqueous solution is not changed by acids or alkalis. The solution in sulphuric acid is blue, becoming yellowish-red on dilution.

Literature.—E. P. 6827 of 1899; D. R. P. 107731; F. P. 280914; A. P. 631611.

Pyramine Orange 3 G (B.):

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_6H_2(NH_2)_2\cdot NO_2 \\ | \\ C_6H_4\cdot N_2\cdot C_6H(SO_3H)_2(NH_2)_2 \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of *m*-phenylenediamine-4 : 6-disulphonic acid and *p*-nitro-*m*-phenylenediamine. The yellowish-red aqueous solution is not changed by acids or alkalis. The solution in sulphuric acid is yellowish-red, becoming brownish-yellow on dilution.

Literature.—E. P. 18506 of 1898; D. R. P. 105349; F. P. 280914; A. P. 631610.

Congo Red (Lev.) (A.) (By.) (L.) (K. S.) (B. K.) (Sch.) (Marden, Orth, and Hastings Corporation); **Congo Red R** (H.); **Cosmos Red** (B.); **Cotton Red conc.** (T. M.); **Cotton Red C** (I.) (P.); **Cotton Red B** (K.); **Dianil Red R** (M.); **Cotton Red 4 B** (O.); **Direct Red C** (Farb werk Ammersfoort):

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2 \\ | \\ C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2 \end{array}$$

Prepared by the action of tetrazotised benzidine on naphthionic acid (2 mols.). It can also be obtained by oxidising benzeneazonaphthionic acid with manganese dioxide in sulphuric acid solution (E. P. 6697 of 1895; D. R. P. 84893; F. P. 248210). The red aqueous solution becomes blue on addition of dilute acids; substance dissolves in sulphuric acid with a slaty blue, giving a bluish precipitate on dilution.

Literature.—E. P. 4415 of 1884; D. R. P. 28753; F. P. 160722; Ber. 1886, 19, 1719.

Diazo Black B (By.). Isomeric with the preceding. Prepared from tetrazotised benzidine and *α*-naphthylamine-5-sulphonic acid (L-acid; 2 mols.). The violet aqueous solution becomes blue with hydrochloric acid, and gives a blue precipitate with sodium hydroxide. The solution in sulphuric acid is blue, remaining blue on dilution. The colouring matter is generally diazotised and developed on the fibre.

Congo Rubine (A.) (Lev.) (By.) (L.) (B. K.); **Azidine Bordeaux** (C. J.); **Congo Rubine A** (K. S.); **Congo Rubine B** (K.); **Cotton Rubine** (B.); **Renol Rubine, extra** (T. M.); **Direct Crimson B** (Sch.):

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2 \\ | \\ C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of *β*-naphthol-8-sulphonic acid and naphthionic acid. The cherry-red aqueous solution gives a blue precipitate with hydrochloric acid and a violet-red one with sodium hydroxide. The solution in sulphuric acid is blue, giving a blue precipitate on dilution.

Literature.—D. R. P. 62659.

Congo Corinth (A.) (By.) (L.) (Lev.) (K. S.) (B. K.); **Cotton Corinth G** (B.) (O.); **Dianil Bordeaux G** (M.); **Renol Corinth G** (T. M.); **Buffalo Garnet R** (Sch.):

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH \\ | \\ C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2 \end{array}$$

Prepared from tetrazotised benzidine, *α*-naphthylamine-4-sulphonic acid and *α*-naphthol-4-sulphonic acid. Aqueous solution red; violet precipitate with hydrochloric acid and colouration with acetic acid. Solution in sulphuric acid blue, giving violet precipitate on dilution.

Literature.—E. P. 15296 of 1885, 2213 of 1886; D. R. P. 39096; F. P. 160722, 163172; A. P. 344971, 358865.

Brilliant Congo G (A.) (L.):

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot NH_2 \\ | \\ C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2 \end{array}$$

From tetrazotised benzidine, *β*-naphthylamine-3 : 6-disulphonic acid and *β*-naphthylamine-6-sulphonic acid (Brönner's). Aqueous solution gives a brownish-violet precipitate with hydrochloric acid. Solution in sulphuric acid blue, giving violet precipitate on dilution.

Literature.—E. P. 6687 of 1887; D. R. P. 41095; F. P. 160722.

Heliotrope 2 B (A.) (By.) (L.):

$$\begin{array}{l} C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH \\ | \\ C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of *α*-naphthol-4 : 8- (or 3 : 8-) disulphonic acid and *β*-naphthol-8-sulphonic acid. Reddish-violet aqueous solution gives a bluish-violet precipitate with hydrochloric acid, and becomes redder with sodium hydroxide. Solution in sulphuric acid is blue, becoming reddish-violet on dilution, and finally giving a violet precipitate.

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[1] **Diamine Scarlet 3 B** (C.), **Dianil Ponceau 2 R** (M.) belongs to the same group, but is bluer.

Literature.—E. P. 1346 of 1888; D. R. P. 45342.

Trisulphone Violet B (K. S.); **Trisulphone Blue R** (K. S.); **Trisulphone Blue B** (K. S.):

$$\begin{array}{l}C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_3{\cdot}OH\\ |\\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH\end{array}$$

The first-named (for which the formula is given) is prepared from tetrazotised benzidine and 1 mol. each of α-naphthol-3 : 6 : 8-trisulphonic acid and β-naphthol. The second and last colouring matters are prepared from tetrazotised tolidine and dianisidine respectively instead of benzidine. The solutions in water are violet to blue, and give bluish-violet to blue precipitates with hydrochloric acid. With sodium hydroxide the aqueous solutions become reddish-violet. The solutions in sulphuric acid are greenish-blue, giving violet precipitates on dilution.

Literature.—E. P. 4703 of 1897; F. P. 264279; A. P. 584981.

Chicago Blue 4 R (A.); **Benzo Blue 4 R** (By.); **Diamine Blue C 4 R** (C.):

$$\begin{array}{l}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(OH){\cdot}SO_3H\\ |\\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(OH)(NH_2){\cdot}SO_3H\end{array}$$

Prepared from benzidine, and 1 mol. each of 1 : 8 aminonaphthol-4-sulphonic acid and β-naphthol-8-sulphonic acid. Violet-blue aqueous solution becomes blue with hydrochloric acid, and reddish-violet with sodium hydroxide. Solution in sulphuric acid is blue, giving a violet precipitate on dilution.

Columbia Blue R (A.); **Benzo Red Blue R** (By.); **Diamine Blue LR** (C.). α-Naphthol-3 : 8-disulphonic acid is used instead of β-naphthol-8-sulphonic acid in the preceding dye. The blue aqueous solution gives a blue precipitate with hydrochloric acid, and is unchanged by sodium hydroxide. Solution in sulphuric acid is blue, giving a violet precipitate on dilution.

Diamine Violet N (C.); **Chlorazol Violet B** (H.); **Dianol Violet N** (Lev.); **Azidine Violet DV** (C. J.); **Naphthamine Violet N** (K.); **Dianil Violet H** (M.); **Direct Violet R** (Sch.); **Benzo Fast Violet NC** (By.):

$$\begin{array}{l}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2\\ |\\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2\end{array}$$

Prepared by the action of tetrazotised benzidine on 2 mols. of 7-amino-α-naphthol-3-sulphonic acid (γ-acid) in acid solution. The reddish-violet aqueous solution gives a violet-black precipitate with hydrochloric acid. The solution in sulphuric acid is greenish-blue, giving a reddish-violet precipitate on dilution.

Literature.—E. P. 16699 of 1889; D. R. P. 55648; F. P. 201770.

Diamine Black RO (C.); **Naphthamine Black BVE** (K.); **Dianol Black RO** (Lev.); **Oxamine Black 2 R** (B.); **Melantherine RO** (I.). Isomeric with the preceding. The combination is effected in alkaline solution whereby the azo- group enters the 2-position with respect to the hydroxy-group, whereas in the preceding case the azo-group enters the 8- position (ortho to the amino- group). The violet-black aqueous solution gives a blue precipitate with hydrochloric acid, and becomes violet with sodium hydroxide. The solution in sulphuric acid is blue, giving a reddish-blue precipitate on dilution.

Literature.—As above.

Naphthamine Black RE (K.):

$$\begin{array}{l}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2\\ |\\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2\end{array}$$

Prepared from tetrazotised benzidine and 2 mols. of 1 : 8-aminonaphthol-6-sulphonic acid.

Literature.—E. P. 515 of 1894; D. R. P. appl. K. 11223; A. P. 563386.

Benzo Violet R (By.):

$$\begin{array}{l}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH\\ |\\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH\end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of α-naphthol-4-sulphonic acid and α-naphthol-3 : 6-disulphonic acid. The reddish-violet aqueous solution gives a soluble violet precipitate with hydrochloric acid, and becomes red with sodium hydroxide. The solution in sulphuric acid is violet, giving a violet precipitate on dilution.

Naphthylamine Diazo Black (K.):

$$\begin{array}{l}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2\\ |\\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2\end{array}$$

Prepared from tetrazotised and benzidine 1 mol. each of 8-amino-α-naphthol-3 : 5-disulphonic acid (K- acid), and 7-amino-α-naphthol-3-sulphonic acid (γ-acid).

Literature.—E. P. 515 of 1894; D. R. P. 99164; A. P. 563386.

Diamine Brown V (C.):

$$\begin{array}{l}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2\\ |\\ C_6H_4{\cdot}N_2{\cdot}C_6H_3(NH_2)_2\end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of 7-amino-α-naphthol-3-sulphonic acid (γ-acid) and *m*-phenylenediamine. Brown-red aqueous solution gives a chocolate-brown precipitate with hydrochloric acid, and purplish-brown precipitate with sodium hydroxide. Solution in sulphuric acid is bluish-violet, giving a purplish-brown precipitate on dilution.

Literature.—E. P. 16699 of 1889; D. R. P. 57857; F. P. 201770.

Dianil Garnet B (M.); **Benzo Fast Red 9 BL** (By.):

$$\begin{array}{l}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2\\ |\\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}NH_2\end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of γ- acid and β-naphthylamine-3 : 6-disulphonic acid. Bordeaux-red aqueous solution gives a blackish-blue precipitate with hydrochloric acid. Solution in sulphuric acid is blue.

Literature.—D. R. P. 190694.

Zambesi Brown G, 2 G (A.):

$$\begin{array}{l}C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(NH_2)_2{\cdot}SO_3H\\ |\\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2\end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of γ- acid and 2 : 7-naphthylenediamine-sulphonic acid. Cotton is dyed corinth brown (G) or violet (2 G).

Literature.—D. R. P. appl. A. 3775.

Diamine Black BH (C.); **Dianol Blue BH** (Lev.); **Diazo Black BHN** (By.); **Renolamine Black BH** (T. M.); **Azidine Black BHN** (C. J.); **Ingrain Black 2 B** (H.); **Naphthamine Black CE** (K.); **Dianil Black ES** (M.); **Melantherine BH** (I.); **Direct Black HB** (L.); **Diazine Black BH extra** (Sch.); **Oxamine Black BHN** (B.); **Direct Black BD** (P.):

$$\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2 \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2 \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of 7-amino-α-naphthol-3-sulphonic acid and 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid). The reddish-blue aqueous solution becomes violet with hydrochloric acid and reddish-violet with sodium hydroxide. The solution in sulphuric acid is blue, giving a violet precipitate on dilution.

Literature.—E. P. 1742 and 6972 of 1891; D. R. P. 68462; F. P. 233032.

Benzo Cyanine R (By.); **Diamine Cyanine R** (C.); **Congo Cyanine R** (A.). Prepared as the preceding, except that 1 : 8-aminonaphthol-4-sulphonic acid is used instead of γ-acid. The solution in water or sulphuric acid is blue. The corresponding **B** marks are prepared from tolidine, and the **3 B** from dianisidine.

Literature.—D. R. P. appl. F. 5667; A. P. 533508, 578432.

Oxamine Violet (B.); **Chlorazol Violet R** (H.); **Naphthamine Violet BE** (K.); **Dianil Violet BE** (M.); **Oxydiamine Violet BF** (C.); **Benzo Violet O** (By.); **Direct Violet O** (I.):

$$\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2 \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2 \end{array}$$

Prepared from tetrazotised benzidine and 6-amino-α-naphthol-3-sulphonic acid (2 mols.). The combination is effected in alkaline solution. The reddish-violet aqueous solution gives a violet precipitate with acids or alkalis. The solution in sulphuric acid is blue, giving a violet precipitate on dilution.

Literature.—E. P. 2614 of 1893; D. R. P. 75469; F. P. 227892; A. P. 521096.

Diamine Blue BB (C.) (Central Dyestuff and Chemical Co.); **Benzo Blue BB** (By.) (Lev.); **Congo Blue 2 BX** (A.); **Direct Blue V** (P.); **Azidine Blue 2 B** (C. J.); **Chlorazol Blue RB** (H.); **Naphthamine Blue 2 BX** (K.); **Dianil Blue HZG** (M.); **Benzamine Blue 2 B** (D.); **Niagara Blue 2 B** (Sch.):

$$\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2 \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2 \end{array}$$

Prepared by combining tetrazotised benzidine in alkaline solution with 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid; 2 mols.). The reddish-blue aqueous solution is unchanged by acids or alkalis. The solution in sulphuric acid is blue, becoming violet on dilution.

Literature.—E. P. 13443 of 1890, 1742 of 1891; D. R. P. 74593; F. P. 210033; A. P. 464135.

Diphenyl Blue Black (G.):

$$\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2 \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH{\cdot}C_6H_5 \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of H-acid and 7-ethylamino-α-naphthol-3-sulphonic acid. The dark-blue aqueous solution gives a violet precipitate with hydrochloric acid, and becomes dark violet with sodium hydroxide. The solution in sulphuric acid is blue, giving a dark violet precipitate on dilution.

Literature.—E. P. 2771 of 1896; D. R. P. 103149; F. P. 250697; A. P. 556164, 567413.

Naphthamine Blues 2B, 3B, and 5B (K.). These are derived from tetrazotised benzidine, tolidine, &c., and 8-amino-α-naphthol-3 : 5-disulphonic acid (K-acid). The blue aqueous solution gives a blue precipitate with hydrochloric acid, and turns reddish-violet with sodium hydroxide. The solution in sulphuric acid is bluish-green.

Literature.—E. P. 515 of 1894; D. R. P. 99164; A. P. 563385, 563386.

Direct Gray R (I.):

$$\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(OH)_2(CO_2H){\cdot}SO_3H \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(OH)_2(CO_2H){\cdot}SO_3H \end{array}$$

Prepared from tetrazotised benzidine and 1 : 7-dihydroxy - 6 - carboxynaphthalene-3-sulphonic acid (2 mols.). The violet aqueous solution gives a bluish-grey precipitate with hydrochloric acid and becomes dull violet-red with sodium hydroxide. The solution in sulphuric acid is blue, giving a bluish-grey precipitate on dilution. The corresponding colour from tolidine is **Direct Gray R.**

Literature.—E. P. 14253 of 1892; D. R. P 75258; F. P. 220468; A. P. 493564.

Direct Violet R (I.).

$$\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_{10}H_3(OH)_2(CO_2H){\cdot}SO_3H \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_7H_5(NH_2)_2 \end{array}$$

Prepared from tetrazotised benzidine and 1 mol. each of the above dihydroxycarboxynaphthalenesulphonic acid and *m*-tolylenediamine. The solution in water is violet, and in sulphuric acid blue.

Literature.—A. P. 527070.

Dianol Red 2 B (Lev.); **Azidine Purpurine 10 B** (C. J.):

$$\begin{array}{l} C_6H_3Cl{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \\ | \\ C_6H_3Cl{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \end{array}$$

Prepared from tetrazotised dichlorobenzidine (NH_2 : Cl=4 : 3), and naphthionic acid (2 mols.). The red aqueous solution becomes violet with hydrochloric acid. The solution in sulphuric acid is blue, changing to violet on dilution.

Literature.—E. P. 25725 of 1896; D. R. P. 94410; F. P. 265135; A. P. 625174, 640743.

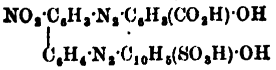
Dianol Brilliant Red extra (Lev.); **Toluylene Red** (O.); **Chlorantine Red 8 B** (I.); **Acetopurpurine 8 B** (A.); **Diphenyl Red 8 B** (G.); **Azidine Brilliant Red 8 B** (C. J.); **Oxamine Scarlet B** (B.):

$$\begin{array}{l} C_6H_3Cl{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}NH_2 \\ | \\ C_6H_3Cl{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}NH_2 \end{array}$$

Prepared from tetrazotised dichlorobenzidine and β-naphthylamine-3 : 6-disulphonic acid. The bluish-red aqueous solution becomes slightly darker with hydrochloric acid. The solution in sulphuric acid is blue, becoming red on dilution.

Literature.—E. P. 25725 of 1896; D. R. P. 94410, 97101; F. P. 265135; A. P. 625174, 640743.

Anthracene Red (I.) (By.)



$$\begin{array}{l}\mathrm{NO_2\cdot C_6H_3\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH}\\ |\\ \mathrm{C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH}\end{array}$$

Prepared by combining tetrazotised nitrobenzidine first with 1 mol. of salicylic acid and then with 1 mol. of *a*-naphthol-4-sulphonic acid. (The same colour is not produced by inverting the order of combination.) The red aqueous solution gives a red precipitate with hydrochloric acid. The solution in sulphuric acid is carmine-red, giving a brownish-red precipitate on dilution.

Literature.—E. P. 13475 of 1892; D. R. P. 72867; F. P. 223176; A. P. 493583.

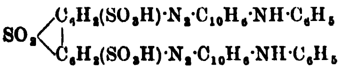
Salicine Red G (K.). Prepared from tetrazotised nitrobenzidine and 1 mol. each of salicylic acid and *β*-naphthol, the product being sulphonated.

Literature.—E. P. 9454 of 1895; D. R. P. 87484.

Salicine Yellow G (K.). Prepared from tetrazotised nitrobenzidine and salicylic acid (2 mols.), the product being sulphonated. The orange aqueous solution is precipitated with hydrochloric acid and becomes reddish-brown with sodium hydroxide. The solution in sulphuric acid is orange-yellow, and gives a brown precipitate on dilution.

Literature.—As above, and Chem. Ind. 1896, 19, 552.

Sulphone Azurine (By.) (A.) (L.) (Lev.):

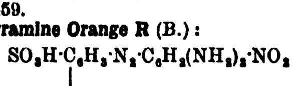


$$\mathrm{SO_2}\left\langle\begin{array}{l}\mathrm{C_6H_2(SO_3H)\cdot N_2\cdot C_{10}H_6\cdot NH\cdot C_6H_5}\\ |\\ \mathrm{C_6H_2(SO_3H)\cdot N_2\cdot C_{10}H_6\cdot NH\cdot C_6H_5}\end{array}\right.$$

Prepared from tetrazotised benzidinesulphonedisulphonic acid and phenyl-*a*-naphthylamine (2 mols.). The blue aqueous solution gives blue precipitates with hydrochloric acid and sodium hydroxide. The solution in sulphuric acid is violet, giving a blackish-violet precipitate on dilution.

Literature.—E. P. 1074 and 1099 of 1884; D. R. P. 27954, 33088; A. P. 432989; Ber. 1889, 22, 2459.

Pyramine Orange R (B.):

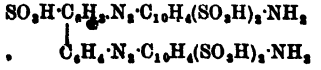


$$\begin{array}{l}\mathrm{SO_3H\cdot C_6H_3\cdot N_2\cdot C_6H_2(NH_2)_2\cdot NO_2}\\ |\\ \mathrm{SO_3H\cdot C_6H_3\cdot N_2\cdot C_6H_2(NH_2)_2\cdot NO_2}\end{array}$$

Prepared from tetrazotised benzidinedisulphonic acid and 6-nitro-*m*-phenylenediamine (2 mols.). The orange-red aqueous solution gives a yellowish-red precipitate with hydrochloric acid or sodium hydroxide. The solution in sulphuric acid is yellow, giving a yellowish-red precipitate on dilution.

Literature.—E. P. 8564 of 1894; D. R. P. 80973; F. P. 238340; A. P. 545333.

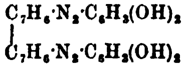
Trypan Red (M.):



$$\begin{array}{l}\mathrm{SO_3H\cdot C_6H_3\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot NH_2}\\ |\\ \mathrm{C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot NH_2}\end{array}$$

Prepared from tetrazotised benzidinemonosulphonic acid and *β*-naphthylamine-3 : 6-disulphonic acid (2 mols.). It is a brown powder, soluble in water, and the solution gives a blue precipitate with hydrochloric acid. It is used in medicine.

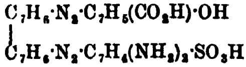
Pyramidol Brown T (Farbwerk Ammersfoort):



$$\begin{array}{l}\mathrm{C_7H_6\cdot N_2\cdot C_6H_3(OH)_2}\\ |\\ \mathrm{C_7H_6\cdot N_2\cdot C_6H_3(OH)_2}\end{array}$$

Prepared from tetrazotised tolidine and resorcinol (2 mols.). The reddish-brown aqueous solution gives a brown precipitate with hydrochloric acid, and becomes brownish-red with sodium hydroxide. The solution in sulphuric acid is violet, giving a blackish-brown precipitate on dilution. When the fibre is treated with diazo- solutions a deep brown is obtained.

Toluylene Orange G (O.) (By.) (A.) (L.); **Azidine Orange G** (C. J.); **Dianil Orange N** (M.); **Alkali Orange GT** (D.); **Renol Orange G** (T. M.); **Direct Orange G** (I.); **Direct Orange Y** (Sch.); **Oxydiamine Orange G** (C.); **Pluto Orange G** (By.); **Direct Orange G** (P.):

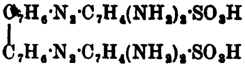


$$\begin{array}{l}\mathrm{C_7H_6\cdot N_2\cdot C_7H_5(CO_2H)\cdot OH}\\ |\\ \mathrm{C_7H_6\cdot N_2\cdot C_7H_4(NH_2)_2\cdot SO_3H}\end{array}$$

Prepared from tetrazotised tolidine and 1 mol. each of hydroxytoluic acid ($\mathrm{CH_3 : OH : CO_2H = 1 : 2 : 3}$) and *m*-tolylenediaminesulphonic acid ($\mathrm{CH_3 : NH_2 : NH_2 : SO_3H = 1 : 2 : 4 : 5}$). The brownish-yellow aqueous solution gives a yellowish-brown precipitate with hydrochloric acid, and becomes reddish-orange with sodium hydroxide. The solution in sulphuric acid is magenta-red, giving a brown precipitate on dilution.

Literature.—E. P. 7997 of 1888; D. R. P. 44797, 47235; A. P. 386634.

Toluylene Orange R (O.) (M.) (L.) (K. S.); **Azidine Orange R** (C. J.); **Alkali Orange RT** (D.); **Renol Orange R** (T. M.); **Direct Orange R** (I.) (Sch.); **Pyramine Orange RT** (B.); **Oxydiamine Orange R** (C); **Pluto Orange R** (By.):

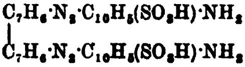


$$\begin{array}{l}\mathrm{C_7H_6\cdot N_2\cdot C_7H_4(NH_2)_2\cdot SO_3H}\\ |\\ \mathrm{C_7H_6\cdot N_2\cdot C_7H_4(NH_2)_2\cdot SO_3H}\end{array}$$

Prepared from tetrazotised tolidine and the above *m*-tolylenediaminesulphonic acid (2 mols.). The orange aqueous solution gives a bluish-red precipitate with hydrochloric acid. The solution in sulphuric acid is brown, giving a reddish precipitate on dilution.

Literature.—E. P. 4492 of 1887; D. R. P. 40905.

Benzopurpurine B (By.) (A.) (L.) (Lev.) (H.) (T. M.) (O.) (Central Dyestuff and Chemical Co.): **Cotton Red B** (I.):



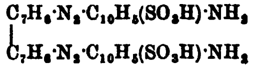
$$\begin{array}{l}\mathrm{C_7H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2}\\ |\\ \mathrm{C_7H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2}\end{array}$$

Prepared by the action of tetrazotised tolidine on *β*-naphthylamine-6-sulphonic acid (2 mols.) in presence of alkali. Aqueous solution, orange-red; unchanged by sodium hydroxide; a brownish-red precipitate by dilute sulphuric acid. Dissolves in sulphuric acid with a blue colour, giving a brown precipitate on dilution.

Literature.—E. P. 3803 of 1885: D. R. P. 35615; A. P. 329633.

Benzopurpurine 4 B (By.) (A.) (Lev.) (T. M.) (L.) (O.) (K. S.) (Farbwerk Ammersfoort) (B. K.)

(Sch.) (H.); **Cotton Red 4 B** (B.) (K.) (I.); **Cotton Red BP** (P.); **Diamine Red 4 B** (C.); **Dianil Red 4 B** (M.); **Direct Red 4 B** (Sch.):



$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \end{array}$$

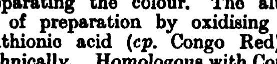
Prepared by the action of tetrazotised tolidine on naphthionic acid (2 mols.). About twice the theoretical amount of naphthionic acid is used, the excess being regained from the filtrate after separating the colour. The alternative method of preparation by oxidising toluene-azonaphthionic acid (*cp.* Congo Red) is not used technically. Homologous with Congo Red, and isomeric with the last. Aqueous solution orange-red, giving a red precipitate with excess of sodium hydroxide; blue precipitate with hydrochloric acid; dissolves in sulphuric acid with a pure blue colour.

Literature.—E. P. 3803 of 1885, 6697 of 1895; D. R. P. 35615, 84893; F. P. 167876, 248210; A. P. 329632.

Benzopurpurine 6 B (Lev.) (By.) (A.) (L.) (T. M.) (O.); **Dianil Red 6 B** (M.); **Cotton Red 6 B** (I.); **Diamine Red 6 B** (C.). Prepared as above from tetrazoditolyl and α-naphthylamine-5-sulphonic acid. Colouring matter very similar in properties to the preceding. The same constitution is assigned to **Diazo Brilliant Black B** (By.), which gives blues or blacks when diazotised and developed on the fibre.

Literature.—E. P. 3803 of 1885; D. R. P. 35615.

Diamine Red B (A.):



$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \end{array}$$

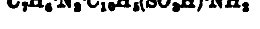
Prepared from tetrazoditolyl and 1 mol. of 2-naphthylamine-7-sulphonic acid and 1 mol. of the 6-sulphonic acid. **Deltapurpurine 5 B** (By.) (A.) (Lev.) (L.) (M.) (B. K.) (K.) (K. S.); **Cotton Purple 5 B** (B.); **Cotton Red D** (I.) is prepared from 2 mols. of the crude β-naphthylamine-δ-sulphonic acid. It is therefore a mixture of Diamine Red B (50 p.c.), Diamine Red 3 B (25 p.c.), and Benzopurpurine B (25 p.c.). Aqueous solution red, giving a brown colouration with acetic acid, and a brown precipitate with hydrochloric acid. Red precipitate with sodium hydroxide. Solution in sulphuric acid blue, giving a brown precipitate on dilution.

Literature.—E. P. 5846 of 1886; D. R. P. 42021; F. P. 180728; Ber. 1887, 20, 1430, 2910, 3160, 3353.

Diamine Red 3 B (A.); **Deltapurpurine 7 B** (Lev.). Isomeric with the preceding. Prepared from tetrazotised tolidine and β-naphthylamine-7-sulphonic acid. The colouring matter is precipitated from its aqueous solution by acetic acid, and forms an insoluble calcium salt. Red precipitate with sodium hydroxide. Solution in sulphuric acid blue, giving brown precipitate on dilution.

Literature.—E. P. 4846 and 12908 of 1886; D. R. P. 41201, 48074; F. P. 178979; Ber. 1887, 20, 2910, 3160.

Rosazurine G (By.) (A.):

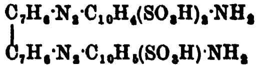


$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH{\cdot}C_2H_5 \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \end{array}$$

Prepared from tetrazotised tolidine and 1 mol each of β-naphthylamine-7-sulphonic acid an ethyl-β-naphthylamine-7-sulphonic acid. Whe 2 mols. of the latter acid are employed th product is known as **Rosazurine B.** Both dye give a cherry-red aqueous solution, which give a reddish-violet precipitate with hydrochlori acid. Their solutions in sulphuric acid ar blue, giving a violet precipitate on dilution.

Literature.—E. P. 17083 of 1886; D. R. P 41761; F. P. 180727.

Brilliant Purpurine R (A.) (By.) (L.):

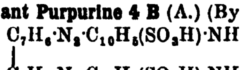


$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}NH_2 \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \end{array}$$

Prepared from tetrazotised tolidine and 1 mol each of β-naphthylamine-3:6-disulphonic aci and naphthionic acid. The red aqueous solutio gives a black precipitate with hydrochloric acid and a red one with sodium hydroxide. The solution in sulphuric acid is blue, giving blue-black precipitate on dilution.

Literature.—E. P. 6687 of 1887; D. R. P 41095; F. P. 160722.

Brilliant Purpurine 4 B (A.) (By.):

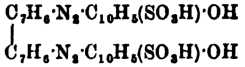


$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \end{array}$$

Prepared from tetrazotised tolidine and 1 mol each of β-naphthylamine-6-sulphonic acid an naphthionic acid. The yellowish-red aqueou solution gives a violet-blue precipitate wit hydrochloric acid. The solution in sulphuri acid is violet-blue, giving a violet-blue precipi tate on dilution.

Literature.—E. P. 15296 of 1885; D. R. P 39096; F. P. 160722.

Azo Blue (By.) (A.) (Lev.); **Benzoin Blue** (B. K.):

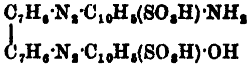


$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH \end{array}$$

Prepared by the action of tetrazotised tolidin on α-naphthol-4-sulphonic acid. Aqueous solu tion of colouring matter violet, becoming crimso on addition of sodium hydroxide; restored t violet by dilute sulphuric acid. Dissolves i sulphuric acid with a pure blue colour, givin violet precipitate on dilution.

Literature.—E. P. 9510 of 1885; D. R. P 35341; F. P. 171133; A. P. 366078.

Congo Corinth B (By.) (A.) (Lev.) (B. K.) (L.) (K. S.); **Cotton Corinth B** (O.); **Reno Corinth B** (T. M.); **Buffalo Violet 4 R** (Sch.) **Dianil Bordeaux B** (M.):

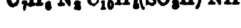


$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH \end{array}$$

From tetrazotised tolidine, naphthionic acid and α-naphthol-4-sulphonic acid. Aqueous solu tion magenta-red, giving violet precipitate wit mineral acids. Blue solution in sulphuric acid violet precipitate on dilution.

Literature.—E. P. 15296 of 1885; 2213 an 6687 of 1886; D. R. P. 39096; A. P. 358865.

Congo Red 4 R (A.) (By.):

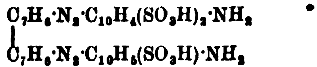


$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_6H_3(OH)_2 \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \end{array}$$

From tetrazotised tolidine, resorcinol, and naphthionic acid. Aqueous solution brownish-red, violet precipitate with mineral acids, brown precipitate with acetic acid. Solution in sulphuric acid blue, giving violet precipitate on dilution.

Literature.—E. P. 15296 of 1885; 2213 of 1886; D. R. P. 39096; F. P. 160722 (addition).

Brilliant Congo R (A.) (By.) (L.); **Brilliant Dianil Red R** (M.); **Azidine Scarlet R** (C. J.):

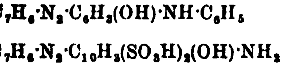


$$\begin{array}{l}\mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}NH_2}\\ |\\ \mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2}\end{array}$$

From tetrazotised tolidine, β-naphthylamine-3 : 6-disulphonic acid and β-naphthylamine-6-sulphonic acid (Brönner's). Aqueous solution brownish-red, giving a similarly coloured precipitate with mineral acids. Solution becomes bluer with acetic acid. Orange precipitate with sodium hydroxide. Blue solution in sulphuric acid, giving dark-brown precipitate on dilution.

Literature.—E. P. 6687 of 1887; D. R. P. 41095.

Azo Black Blue B, R (O.):

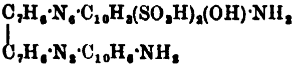


$$\begin{array}{l}\mathrm{C_7H_6{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}NH{\cdot}C_6H_5}\\ |\\ \mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2}\end{array}$$

Prepared from tetrazotised tolidine and 1 mol. each of *m*-hydroxydiphenylamine and 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid). Solution in water is brownish-violet and in sulphuric acid blue, giving a bluish-violet precipitate on dilution.

Literature.—E. P. 10861 of 1891; D. R. P. 70201; A. P. 402415.

Azo Mauve B (O.):

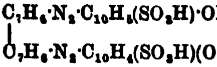


$$\begin{array}{l}\mathrm{C_7H_6{\cdot}N_6{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2}\\ |\\ \mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2}\end{array}$$

Prepared from tetrazotised tolidine and 1 mol. each of 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid) and α-naphthylamine. Violet aqueous solution gives a violet precipitate with hydrochloric acid, and becomes rather bluer with dilute acetic acid. Solution in sulphuric acid is blue, becoming violet on dilution. When β-naphthylamine is used instead of the α-compound the product is **Naphthazurine B** (O.), the reactions of which are similar to the above.

Literature.—As above and A. P. 462415, 608999.

Chicago Blue 2 R (A.); **Benzo Blue 2 R** (By.); **Diamine Blue C 2 R** (C.); **Azidine Wool Blue R** (C. J.):

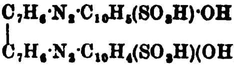


$$\begin{array}{l}\mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH}\\ |\\ \mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2}\end{array}$$

Prepared from tetrazotised tolidine and 1 mol. each of β-naphthol-8-sulphonic acid and 8-amino-α-naphthol-5-sulphonic acid. The violet-blue aqueous solution gives a dark-blue precipitate with hydrochloric acid, and becomes reddish-violet with sodium hydroxide. Solution in sulphuric acid is blue, giving a blue precipitate on dilution. The corresponding colour from dianisidine is **Azidine Wool Blue B** (C. J.).

Literature.—E. P. 27609 of 1907; D. R. P. 203535, 209269; F. P. 383747; A. P. 888036.

Oxamine Blue 4 R (B.); **Azidine Blue 3 RN** (C. J.); **Naphthamine Blue 3 RE** (K.); **Dianil Azurine 3 R** (M.); **Benzoazurine 3 R** (By.) (O.):

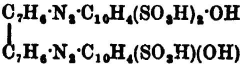


$$\begin{array}{l}\mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH}\\ |\\ \mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2}\end{array}$$

Prepared from tetrazotised tolidine and 1 mol. each of 6-amino-α-naphthol-3-sulphonic acid and α-naphthol-4-sulphonic acid. Violet aqueous solution is precipitated with hydrochloric acid or sodium hydroxide. Solution in sulphuric acid is blue, giving a violet precipitate on dilution.

Literature.—E. P. 2614 of 1893; D. R. P. 93276; F. P. 227892; A. P. 521095.

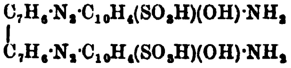
Columbia Blue G (A.); **Benzo Red Blue G** (By.); **Diamine Blue LG** (C.):



$$\begin{array}{l}\mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH}\\ |\\ \mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2}\end{array}$$

Prepared from tetrazotised tolidine and 1 mol. each of α-naphthol-3 : 8-disulphonic acid and 8-amino-α-naphthol-5-sulphonic acid. Blue aqueous solution gives a blue precipitate with hydrochloric acid, and a reddish-violet one with sodium hydroxide. Solution in sulphuric acid is greenish-blue, giving a reddish-violet precipitate on dilution.

Chicago Blue R (A.) (By.); **Diamine Blue CR** (C.):

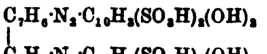


$$\begin{array}{l}\mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2}\\ |\\ \mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2}\end{array}$$

Prepared from tetrazotised tolidine and 8-amino-α-naphthol-5-sulphonic acid (2 mols.). The violet-blue solution gives a dark-violet precipitate with hydrochloric acid. The solution in sulphuric acid is cornflower blue, giving a bluish-violet precipitate on dilution. The corresponding colour from dianisidine is **Chicago Blue B** (A.) (By.); **Diamine Blue CB** (C.).

Literature.—A. P. 506284.

Dianil Blue B (M.):

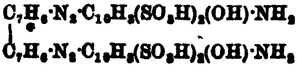


$$\begin{array}{l}\mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH)_2}\\ |\\ \mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH)_2}\end{array}$$

Prepared from tetrazotised tolidine and 2 mols. of 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid (chromotrope acid). The blue aqueous solution is not changed with hydrochloric acid or sodium hydroxide. The solution in sulphuric acid is deep-blue, becoming bluish-violet on dilution.

The corresponding colour from benzidine is **Dianil Blue R**, and from dianisidine **Dianil Blue G**, and when 1 mol. each of chromotrope acid and α-naphthol-4-sulphonic acid are used the product is **Dianil Blue 2 R** (M.); **Naphthamine Brilliant Blue 2 R** (K.); **Benzo New Blue 2 B** (By.).

Diamine Blue 3 B (C.); **Benzo Blue 3 B** (By.); **Congo Blue 3 B** (A.) (Lev.); **Azidine Blue 3 B** (C. J.); **Chlorazol Blue 3 B** (H.); **Naphthamine Blue 3 BX** (K.); **Dianil Blue H 3 G** (M.); **Benzamine Blue 3 B** (D.); **Niagara Blue 3 B** (Sch.):



$$\begin{array}{l}\mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2}\\ |\\ \mathrm{C_7H_6{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2}\end{array}$$

Prepared from tetrazotised tolidine and 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid; 2 mols.). When used in medicine it is known as **Trypan Blue** (M.). The violet aqueous solution becomes bluer with hydrochloric acid, and gives a precipitate with excess. The solution in sulphuric acid is blue, giving a violet precipitate on dilution.

Literature.—E. P. 13443 of 1890; 1742 of 1891; D. R. P. 74593; F. P. 201770, 210033.

Eboli Blue B (L.). Isomeric with the above, 8-amino-α-naphthol-4 : 6-disulphonic acid being used instead of H-acid. The blue aqueous solution gives a blue precipitate with hydrochloric acid, and becomes reddish-violet with sodium hydroxide. The solution in sulphuric acid is blue.

Literature.—E. P. 19253 of 1895; D. R. P. appl. F. 8626; A. P. 606436, 606437, 606438, 606439.

Diamine Blue BX (C.); **Benzo Blue BX** (By.); **Congo Blue BX** (A.) (Lev.); **Azidine Blue BX** (C. J.); **Naphthamine Blue BXR** (K.); **Dianil Blue HG** (M.); **Eboli New Blue 2 B** (L.); **Benzamine Blue BX** (D.); **Niagara Blue BX** (Sch.):

$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2 \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH \end{array}$$

Prepared from tetrazotised tolidine and 1 mol. each of α-naphthol-4-sulphonic acid and 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid). The bluish-violet aqueous solution gives a violet precipitate with hydrochloric acid, and becomes bluish-red with sodium hydroxide. The solution in sulphuric acid is blue, giving a violet precipitate on dilution.

Literature.—E. P. 1742 of 1891; D. R. P. 74593; F. P. 201770 addition.

Direct Blue R (I.).

$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_3(CO_2H)(OH)_2{\cdot}SO_3H \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH \end{array}$$

Prepared from tetrazotised tolidine and 1 mol. each of 1 : 7-dihydroxy-6-carboxynaphthalene-3-sulphonic acid and α-naphthol-4-sulphonic acid. The violet aqueous solution gives a violet precipitation with hydrochloric acid, and becomes violet-red with sodium hydroxide. The solution in sulphuric acid is blue. The corresponding colour from dianisidine is **Direct Blue B** (I.).

Literature.—E. P. 14161 and 14253 of 1892; D. R. P. 67000, 75258; F. P. 219875, 220468; A. P. 493563, 493564.

Indazurine RM (I.). Isomeric with the preceding. A different naphthoic acid, viz.: 1 : 7-dihydroxy-2 - carboxynaphthalene - 4 - sulphonic acid is used, the other constituents being the same. The violet-blue aqueous solution becomes bluer with hydrochloric acid and red with sodium hydroxide. The solution in sulphuric acid is blue, giving a violet precipitate on dilution. The corresponding colour from dianisidine is **Indazurine GM** (I.).

Literature.—A. P. 524070.

Indazurine TS (I.):

$$\begin{array}{l} C_7H_6{\cdot}N_2{\cdot}C_{10}H_3(CO_2H)(OH)_2{\cdot}SO_3H \\ | \\ C_7H_6{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2 \end{array}$$

Prepared as the preceding, except that 7-amino-α-naphthol-3-sulphonic acid is used instead of α-naphthol-4-sulphonic acid. The violet-blue aqueous solution becomes redder with acids or alkalis. The solution in sulphuric acid is blue, giving a violet precipitate on dilution.

Literature.—As above.

Milling Scarlet 4 R (M.); **Acid Anthracene Red 3 B** (By.); **Florida Red R** (L.):

$$\begin{array}{l} HSO_3{\cdot}C_7H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH \\ | \\ HSO_3{\cdot}C_7H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH \end{array}$$

Prepared from tetrazotised tolidinodisulphonic acid and β-naphthol (2 mols.). The carmoisine-red aqueous solution gives a violet precipitate with hydrochloric acid. The solution in sulphuric acid is violet-red.

Diamine Yellow N (C.):

$$\begin{array}{l} C_2H_5{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}O{\cdot}C_2H_5 \end{array}$$

Prepared by combining tetrazotised ethoxybenzidine first with salicylic acid (1 mol.) and then with phenol (1 mol.) and ethylating the product. The yellow aqueous solution gives a greenish precipitate with hydrochloric acid and a reddish-yellow with sodium hydroxide. The solution in sulphuric acid is violet, giving a greenish-brown precipitate on dilution.

Literature.—E. P. 14464 of 1887; D. R. P. 46134; F. P. 186566, 186567; A. P. 380067.

Diamine Blue 3 R (C.):

$$\begin{array}{l} C_2H_5{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH \end{array}$$

Prepared from tetrazotised ethoxybenzidine and α-naphthol-4-sulphonic acid (2 mols.). The reddish-blue aqueous solution is not changed with hydrochloric acid, but becomes reddish-violet with sodium hydroxide. The solution in sulphuric acid is dark-blue, giving a violet precipitate on dilution.

Literature.—As above.

Diamine Blue B (C.):

$$\begin{array}{l} C_2H_5{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH \\ | \\ C_6H_4\ N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH \end{array}$$

Prepared from tetrazotised ethoxybenzidine and 1 mol. each of β-naphthol-3 : 7-disulphonic acid and α-naphthol-4-sulphonic acid. The blue aqueous solution gives a blue precipitate with hydrochloric acid, and becomes reddish-blue with sodium hydroxide. The solution in sulphuric acid is blue, giving a blue precipitate on dilution.

Literature.—As above.

Diamine Blue Black E (C.):

$$\begin{array}{l} C_2H_5{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH \\ | \\ C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2 \end{array}$$

Prepared as the preceding, except that 7-amino α-naphthol-3-sulphonic acid is used instead o α-naphthol-4-sulphonic acid. The combinatio is effected in alkaline solution. The blackish-blue aqueous solution gives a blue precipitate with hydrochloric acid, and is not changed with sodium hydroxide. The solution in sulphuric acid is blackish-blue, giving a blue precipitate on dilution.

Literature.—E. P. 16699 of 1889; D. R. P. 57857; F. P. 201770.

Diazurine B (By.):

$$\begin{array}{l}CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2\\ \quad\;|\\ CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2\end{array}$$

Prepared from tetrazotised dianisidine and α-naphthylamine-6-(or 7-)sulphonic acid (Cleve's acid) (2 mols.). The brownish-red aqueous solution gives a blue precipitate with hydrochloric acid and a soluble red one with sodium hydroxide. The solution in sulphuric acid is blue, giving a blue precipitate on dilution.

Literature.—D. R. P. 65262.

Benzopurpurine 10 B (By.) (Lev.) (K.) (L.) (A.) (O.) (K. S.) (T. M.); **Dianil Red 10 B** (M.); **Cotton Red 10 B** (I.) (P.); **Diamine Red 10 B** (C.); **Buffalo Cardinal 7 B** (Sch.). Isomeric with the preceding. Prepared from tetrazotised dianisidine and 2 mols. of naphthionic acid. The carmine-red aqueous solution gives a blue precipitate with hydrochloric acid and a red one with sodium hydroxide. The solution in sulphuric acid is blue, giving a blue precipitate on dilution.

Literature.—E. P. 14424 of 1885; D. R. P. 38802; F. P. 173042; A. P. 481954.

Azo- Violet (By.) (A.) (L.) (Lev.):

$$\begin{array}{l}CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot NH_2\\ \quad\;|\\ CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_5(SO_3H)\ OH\end{array}$$

Tetrazotised dianisidine (1 mol.) is combined with 1 mol. of naphthionic acid, and then with 1 mol. of α-naphthol-4-sulphonic acid. Aqueous solution reddish-violet, giving blue precipitate with mineral acids and bluish-violet colouration with acetic acid. Solution turned magenta by sodium hydroxide. Dissolves with a blue colour in sulphuric acid, giving a blue precipitate on dilution.

Literature.—E. P. 14424 of 1885; 7283 of 1886; D. R. P. 40247; F. P. 173042; A. P. 447302.

Benzoazurine G (By.) (A.) (L.) (Lev.) (K.) (O.) (K. S.); **Dianil Azurine G** (M.); **Renol Blue B** (T. M.); **Cotton Blue 3 G** (I.); **Benzoin Blue GN, 2GN, 5GN** (B. K.); **Direct Blue G extra** (Sch.); **Oxamine Blue A** (B.); **Azidine Blue BA** (C. J.):

$$\begin{array}{l}CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH\\ \quad\;|\\ CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH\end{array}$$

Prepared by the action of tetrazotised dianisidine on α-naphthol-4-sulphonic acid. Aqueous solution bluish-violet, becoming red on addition of sodium hydroxide; dark-violet precipitate with dilute hydrochloric acid. Dissolves in sulphuric acid with a blue colour, giving violet precipitate on dilution. **Benzoazurine R** (By.) (A.) (L.) (O.) is a mixture of benzoazurine G and azo blue.

Literature.—E. P. 14424 of 1885; D. R. P. 38802; F. P. 173042; A. P. 357273, 481954.

Benzoazurine 3 G (By.) (A.) (L.) (Lev.) (K.). Isomeric with the above. α-Naphthol-5-sulphonic acid (Laurent's acid) is used instead of the 4-sulphonic acid. Aqueous solution bluish-violet, giving bluish-violet precipitate with hydrochloric acid and becoming violet-red with sodium hydroxide. Solution in sulphuric acid is blue, giving violet precipitate on dilution.

Literature.—As above.

Congo Blue 2 B (By.):

$$\begin{array}{l}CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH\\ \quad\;|\\ CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH\end{array}$$

Prepared from tetrazotised dianisidine and 1 mol. each of β-naphthol-3 : 6-disulphonic acid and α-naphthol-4-sulphonic acid. Blue aqueous solution gives a dark-blue precipitate with hydrochloric acid, and becomes magenta-red with sodium hydroxide. Solution in sulphuric acid is blue, giving a blue precipitate on dilution.

Literature.—E. P. 7283 of 1886; D. R. P. 40247; F. P. 173042 (addition); A. P. 467162.

Chlorazol Blue R and 3 G (H.):

$$\begin{array}{l}CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_4Cl(SO_3H)\cdot OH\\ \quad\;|\\ CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_4Cl(SO_3H)\cdot OH\end{array}$$

Prepared from tetrazotised dianisidine and 2 mols. of chloro-α-naphthol-5- and -4-sulphonic acids respectively. The violet aqueous solution undergoes little change with hydrochloric acid, but turns crimson with sodium hydroxide. The solution in sulphuric acid is greenish-blue (R) or green (3 G).

Literature.—E. P. 12085 of 1898.

Diamine Brilliant Blue G (C.):

$$\begin{array}{l}CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_3Cl(SO_3H)_2\cdot OH\\ \quad\;|\\ CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_3Cl(SO_3H)_2\cdot OH\end{array}$$

Prepared from tetrazotised dianisidine and 2 mols. of 8-chloro-α-naphthol-3 : 6-disulphonic acid. Bluish-violet aqueous solution gives a soluble violet precipitate with hydrochloric acid, and becomes cherry-red with sodium hydroxide. Solution in sulphuric acid is greenish-blue, turning violet on dilution.

Literature.—E. P. 1920 of 1894; D. R. P. 79055, 82285; F. P. 235271; A. P. 532125, 535037.

Oxamine Blue B (B.):

$$\begin{array}{l}CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH\\ \quad\;|\\ CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2\end{array}$$

Prepared from tetrazotised dianisidine and 1 mol. each of 5-amino-α-naphthol-3-sulphonic acid and α-naphthol-4-sulphonic acid. Dark-blue aqueous solution turns reddish-violet with sodium hydroxide, and pale violet with hydrochloric acid. The solution in sulphuric acid is bluish-green, becoming violet on dilution.

Literature.—E. P. 2370 of 1893; D. R. P. 82572; F. P. 229263; A. P. 558344.

Chicago Blue 6 B (A.); **Brilliant Benzo Blue 6 B** (By.); **Diamine Sky Blue FF** (C.); **Azidine Sky Blue FF** (C. J.); **Chlorazol Sky Blue FF** (H.); **Dianol Brilliant Blue 6 B** (Lev.); **Oxamine Sky Blue 6 B** (B.); **Dianil Sky Blue PH** (M.):

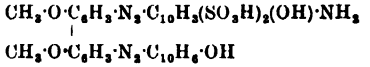
$$\begin{array}{l}CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)\cdot NH_2\\ \quad\;|\\ CH_3\cdot O\cdot C_6H_3\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)\cdot NH_2\end{array}$$

Prepared from tetrazotised dianisidine and 2 mols. of 8-amino-α-naphthol-5 : 7-disulphonic acid (S-acid). The combination is effected in alkaline solution. Blue aqueous solution is not changed with hydrochloric acid, but becomes bluish-violet with sodium hydroxide. Solution in sulphuric acid is bluish-green, becoming pure blue on dilution.

Diamine Sky Blue (C.) ; **Benzo Sky Blue** (By.) ; **Congo Sky Blue** (A.) ; **Dianol Sky Blue** (Lev.) ; **Renol Pure Blue** (T. M.) ; **Azidine Sky Blue** (C. J.) ; **Chlorazol Blue 6 G** (H.) ; **Naphthamine Blue 7 B** (K.) ; **Dianil Blue H 6 G** (M.) ; **Oxamine Sky Blue 5 B** (B.) ; **Benzamine Sky Blue** (D.) ; **Benzoin Sky Blue** (B. K.) ; **Direct Blue RBA** (L.) ; **Niagara Blue 4 B** (Sch.). Isomeric with the preceding. Two mols. of 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid) are used as components. Blue aqueous solution is not changed with hydrochloric acid, but becomes redder with sodium hydroxide. Solution in sulphuric acid is bluish-green, becoming pure blue on dilution.

Literature.—E. P. 1742 of 1891 ; D. R. P. 74593 ; F. P. 201770 ; A. P. 464135.

Chicago Blue RW (A.) ; **Benzo Blue RW** (By.) ; **Diamine Blue RW** (C.) ; **Dianol Blue RW** (Lev.) :

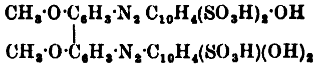


$$\begin{array}{l}\mathrm{CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2}\\ \quad\quad\vert\\ \mathrm{CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH}\end{array}$$

Prepared from tetrazotised dianisidine and 1 mol. each of 8-amino-α-naphthol-5 : 7-disulphonic acid and β-naphthol. Blue aqueous solution gives a blue precipitate with hydrochloric acid, and becomes violet with sodium hydroxide. Solution in sulphuric acid is green, giving a violet precipitate on dilution.

Chicago Blue 4 B (A.) ; **Benzo Sky Blue 4 B** (By.) ; **Diamine Sky Blue C 4 B** (C.). Instead of β-naphthol in the preceding colouring matter, 8-amino-α-naphthol-5-sulphonic acid is used. Blue aqueous solution gives a bluish-violet precipitate with hydrochloric acid, and is unchanged with sodium hydroxide. Solution in sulphuric acid is bluish-green, giving a blue precipitate on dilution.

Indazurine B (I.) :

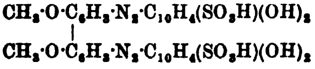


$$\begin{array}{l}\mathrm{CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2\,C_{10}H_4(SO_3H)_2{\cdot}OH}\\ \quad\quad\vert\\ \mathrm{CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH)_2}\end{array}$$

Prepared from tetrazotised dianisidine and 1 mol. each of 1 : 7-dihydroxynaphthalene-4-sulphonic acid and β-naphthol-3 : 6-disulphonic acid. Blue aqueous solution turns bluer with hydrochloric acid and red with sodium hydroxide. Solution in sulphuric acid is blue, giving a reddish-blue precipitate on dilution. When *m*-tolylenediamine is used instead of R-salt the colour produced is called **Direct Violet BB** (I.). The violet aqueous solution shows the same reactions as the above, as does also the solution in sulphuric acid.

Literature.—D. R. P. 524069 ; A. P. 524069.

Brilliant Azurine 5 G (By.) (A.) (L.) :

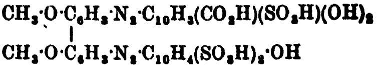


$$\begin{array}{l}\mathrm{CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH)_2}\\ \quad\quad\vert\\ \mathrm{CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH)_2}\end{array}$$

Prepared by combining tetrazotised dianisidine with 2 mols. of 1 : 8-dihydroxynaphthalene-4-sulphonic acid in acetic acid solution. Aqueous solution is bluish-violet ; with hydrochloric acid gives a blue precipitate, and with sodium hydroxide becomes red. Solution in sulphuric acid is greenish-blue, giving a dark reddish-blue precipitate on dilution.

Literature.—E. P. 14424 of 1885 ; 13665 of 1889 ; D. R. P. 57166 ; F. P. 173042 ; A. P. 417294.

Indazurine BB (I.) :

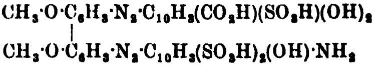


$$\begin{array}{l}\mathrm{CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_3(CO_2H)(SO_3H)(OH)_2}\\ \quad\quad\vert\\ \mathrm{CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)_2{\cdot}OH}\end{array}$$

Prepared from tetrazotised dianisidine and 1 mol. each of 1 : 7-dihydroxy-2-carboxynaphthalene-4-sulphonic acid and β-naphthol-3 : 6-disulphonic acid (R-salt). Blue aqueous solution becomes slightly bluer with hydrochloric acid, and redder with sodium hydroxide. Solution in sulphuric acid is greenish-blue, giving a blue precipitate on dilution.

Literature.—A. P. 524070.

Indazurine 5 GM (I.) :

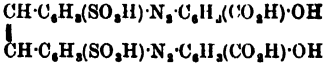


$$\begin{array}{l}\mathrm{CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_3(CO_2H)(SO_3H)(OH)_2}\\ \quad\quad\vert\\ \mathrm{CH_3{\cdot}O{\cdot}C_6H_3{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2}\end{array}$$

Prepared as the preceding, except that 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid) is used instead of R-salt. The pure blue aqueous solution is not changed with hydrochloric acid, but becomes redder with sodium hydroxide. The solution in sulphuric acid is bluish-green, becoming bluish-violet on dilution.

Literature.—As above.

Hessian Yellow (L.) :

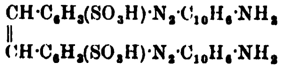


$$\begin{array}{l}\mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH}\\ \Vert\\ \mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH}\end{array}$$

Prepared from tetrazotised diaminostilbenedisulphonic acid[1] and salicylic acid. Aqueous solution ochreous, giving blackish precipitate with mineral acids. Solution reddened by sodium hydroxide. Reddish-violet solution in sulphuric acid, giving blackish precipitate on dilution.

Literature.—E. P. 4387 of 1886 ; D. R. P. 38735 ; A. P. 350299, 350230.

Hessian Purple N (L.) (By.).

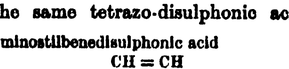


$$\begin{array}{l}\mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2}\\ \Vert\\ \mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2}\end{array}$$

From tetrazotised diaminostilbenedisulphonic acid and β-naphthylamine. Aqueous solution red, giving bluish-black precipitate with mineral acids, and violet-black precipitate with acetic acid. Red colouration or precipitate with sodium hydroxide. Blue solution in sulphuric acid, giving bluish-black precipitate on dilution.

References as in preceding.

Brilliant Yellow (L.) (A.) (By.) :

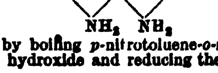


$$\begin{array}{l}\mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_6H_4{\cdot}OH}\\ \Vert\\ \mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_6H_4{\cdot}OH}\end{array}$$

From the same tetrazo-disulphonic acid and

---

[1] Diaminostilbenedisulphonic acid

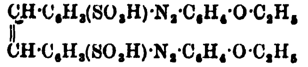


is prepared by boiling *p*-nitrotoluene-*o*-sulphonic acid with sodium hydroxide and reducing the product with zinc-dust.

phenol. Aqueous solution orange, giving violet precipitate with mineral acids. Dissolves with a reddish-violet in sulphuric acid, giving a violet precipitate on dilution.

References as in preceding.

Chrysophenine G (K. S.) (L.) (A.) (By.); **Chrysobarine G extra conc.** (T. M.); **Phenine Yellow** (P.); **Azidine Yellow CP** (C. J.); **Direct Yellow CRG** (L.); **Aurophenine O** (M.); **Pyramine Yellow G** (B.); **Triazol Yellow G** (O.):

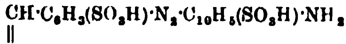


$$\begin{array}{l}\mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_6H_4{\cdot}O{\cdot}C_2H_5}\\ \|\\ \mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_6H_4{\cdot}O{\cdot}C_2H_5}\end{array}$$

Prepared by ethylating the preceding colouring matter. Aqueous solution orange, giving brown precipitate with mineral acids. Dissolves with a reddish-violet colour in sulphuric acid, giving blue precipitate on dilution.

Literature.—E. P. 3994 of 1887; D. R. P. 42466; F. P. 182063; Ber. 1894, 27, 3357; 1903, 36, 2975.

Hessian Brilliant Purple (L.)



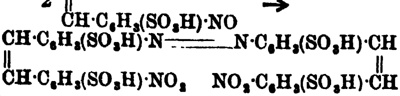
$$\begin{array}{l}\mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2}\\ \|\\ \mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2}\end{array}$$

Prepared from tetrazotised diaminostilbenedisulphonic acid, and 2 mols. of β-naphthylamine-6-sulphonic acid. Purple-red aqueous solution gives bluish-black precipitate with hydrochloric acid and carmine-red precipitate with sodium hydroxide. Solution in sulphuric acid blue, giving a bluish-black precipitate on dilution.

References as for Hessian Yellow.

Stilbene Colouring Matters.

The colouring matters which have hitherto been classified under this head are produced by alkaline condensation and oxidation of *p*-nitrotoluenesulphonic acid under various conditions. They have generally been considered to be nitroso- or azoxy- stilbene derivatives, but the recent researches of A. G. Green and his collaborators have shown that all the colouring matters of this group must be regarded as azo-dyes (Chem. Soc. Trans. 1904, 85, 1424, 1432; 1906, 89, 1602; 1907, 91, 2076; 1908, 93, 1721; J. Soc. Dyers, 1907, 23, 162). The first action of alkali hydroxide on *p*-nitrotoluenesulphonic acid leads to the formation of a dinitrosostilbenedisulphonic acid, one molecule of which is oxidised at the expense of a second molecule, and the remaining two nitrogen atoms of two molecules combine to form an azo- group in a distilbene molecule:

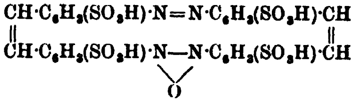


$$2\begin{array}{l}\mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}NO}\\ \|\\ \mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}NO}\end{array}\rightarrow$$

$$\begin{array}{lcr}\mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}N} & \text{——————} & \mathrm{N{\cdot}C_6H_3(SO_3H){\cdot}CH}\\ \| & & \|\\ \mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}NO_2} & & \mathrm{NO_2{\cdot}C_6H_3(SO_3H){\cdot}CH}\end{array}$$

The equation represents the formation of the greenest yellow of the series (stilbene yellow 8G: *see* below). The redder yellows and oranges may be regarded as formed therefrom by the reduction of the two nitro- groups, first to an azoxy- and finally to an azo- group.

Sun Yellow (G.) (K. S.); **Afghan Yellow** (H.); **Curcumine S** (L.) (A.); **Direct Yellow J** (P.); **Azidine Fast Yellow G** (C. J.); **Direct Yellow RT** (Cl. Co.); **Direct Yellow F** (Sch.); **Direct Yellow G** (I.); **Direct Yellow R** (P.) (O.); **Diamine Fast Yellow A** (C.). Prepared by heating *p*-nitrotoluenesulphonic acid with aqueous sodium hydroxide. Direct yellow RT, which was analysed by Green (*l.c.*), is considered to have the constitution.



(the colouring matter being, of course, the sodium salt).

Aqueous solution is brownish-yellow. Solution in sulphuric acid is violet, becoming yellow on dilution.

Literature.—E. P. 4387 of 1886; D. R. P. 38735; F. P. 175630; A. P. 360553; Bull. Mulhouse, 1887, 99; Ber. 1886, 19, 3234.

Naphthamine Yellow G (K.); **Direct Yellow R** (By.); **Renol Yellow R** (T. M.). Prepared as above, but the temperature of the reaction is 60°–85°. Reddish-yellow aqueous solution gives brown precipitate with excess of hydrochloric acid and a yellow precipitate with sodium hydroxide. Solution in sulphuric acid is cherry-red, becoming yellow on dilution.

Literature.—E. P. 23672 of 1892; D. R. P. 79241; F. P. 226635; Ber. 1893, 26, 2233; 1895, 28, 2281.

Mikado Yellow (A.); **Mikado Yellow G** (L.); **Mikado Gold Yellow 2 G, 4 G, 6 G, 8 G** (L.); **Naphthamine Yellow 2 G, 3 G** (K.); **Renol Yellow 2 G** (T. M.); **Dianil Direct Yellow S** (M.); **Formal Yellow** (G.); **Stilbene Yellow 3 G** (B.); **Paper Yellow** (M.). Prepared by treating the products of condensation of *p*-nitrotoluenesulphonic acid and sodium hydroxide with oxidising agents. Yellow aqueous solution gives a brownish-yellow precipitate with hydrochloric acid, and yellow solution or precipitate with sodium hydroxide. Solution in sulphuric acid is orange to red, becoming yellow on dilution.

Literature.—E. P. 23672 of 1892; D. R. P. 42466; F. P. 226635; Ber. 1893, 26, 2234; 1897, 30, 2618, 3097; 1898, 31, 354, 1078.

Stilbene Yellow G, 4 G, 6 G, 8 G (Cl. Co.). The constitution of the last brand has already been given. The colouring matters are alkaline condensation products of dinitrodibenzyldisulphonic acid, and dinitrostilbenedisulphonic acid. Solution in sulphuric acid is orange to yellowish-red, becoming yellow on dilution.

Literature.—E. P. 5351, 21553, 21399, of 1897; 3393 of 1898; D. R. P. 96107, 113513, 113514; F. P. 272384, 273018, 273037; Ber. 1897, 30, 3097; 1898, 31, 1087.

Diphenylcitronine G (G.). Prepared by condensing dinitrodibenzyldisulphonic acid with aniline in presence of sodium hydroxide or by condensing similarly dinitrostilbenedisulphonic acid. Yellow aqueous solution gives a brownish-yellow precipitate with hydrochloric acid, and an orange-yellow one with sodium hydroxide. Solution in sulphuric acid is orange, giving a brownish-yellow precipitate on dilution.

Literature.—E. P. 18990, 21399, 21553 of 1897; D. R. P. 101760, 113514; F. P. 269466, 273018; A. P. 613911.

Diphenyl Fast Yellow (G.). Prepared by condensing dinitrodibenzyldisulphonic acid or dinitrostilbenedisulphonic acid with primuline or dehydrothio-*p*-toluidinesulphonic acid in presence of sodium hydroxide. Yellow aqueous solution gives a brownish-orange yellow precipitate with hydrochloric acid, and an orange-yellow one with sodium hydroxide. Solution in sulphuric acid is red, giving a brownish-yellow precipitate on dilution.

Literature.—E. P. 18990, 21399, 21553 of 1897; D. R. P. 100613, 113514; F. P. 269406, 273018.

Mikado Brown B, 3 GO, M (L.). Prepared by the action of alkalis on *p*-nitrotoluenesulphonic acid in presence of oxidisable substances. Brown aqueous solution gives a brown precipitate with hydrochloric acid. Solution in sulphuric acid is violet-black, giving a brown precipitate on dilution.

Literature.—E. P. 2664 of 1888; D. R. P. 46252, 48528; F. P. 189697; A. P. 395115, 396527.

Mikado Orange G to **5 R** (L.); **Naphthamine Orange 2 R** (K.); **Direct Orange G** (G.); **Chloramine Orange G** (By.); **Stilbene Orange 4 R** (Cl. Co.); **Stilbene Yellow 3 G** (B.). Prepared by the same reaction as the preceding, and by the action of alkaline reducing agents on direct yellow. Orange-yellow aqueous solution gives a dark-brown precipitate with hydrochloric acid, and an orange one with sodium hydroxide. Solution in sulphuric acid is violet to blue, giving a brown precipitate on dilution.

Mikado Orange 3 RO (L.) has the constitution

$$\begin{array}{l} CH\cdot C_6H_3(SO_3H)\cdot N:N\cdot C_6H_3(SO_3H)\cdot CH \\ \| \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \| \\ CH\cdot C_6H_3(SO_3H)\cdot N:N\cdot C_6H_3(SO_3H)\cdot CH \end{array}$$

Brands 4 RO and 5 RO are redder shades.

Literature.—E. P. 2664 of 1888; D. R. P. 46252, 48528, 96929; F. P. 189697; A. P. 395115, 396527; Ber. 1893, 26, 2233; 1895, 28, 2281.

Polychromine B (G.); **Fast Cotton Brown R** (G.); **Direct Brown R** (G.). Prepared by boiling equal molecules of *p*-nitrotoluenesulphonic acid and *p*-phenylenediamine with sodium hydroxide. Orange-brown aqueous solution gives a blue-black precipitate with hydrochloric acid. Solution in sulphuric acid is reddish-violet, giving a bluish-black precipitate on dilution.

Literature.—E. P. 15671 of 1890; D. R. P. 59290; F. P. 208626; A. P. 455952.

Diphenyl Orange RR (G.); **Azidine Orange D 2 R** (C. J.). Prepared by condensing 2 mols. of *p*-nitrotoluenesulphonic acid with 2 mols. of *p*-phenylenediamine in presence of concentrated aqueous sodium hydroxide. Orange-yellow aqueous solution gives a bluish-black precipitate with hydrochloric acid, and an orange one with sodium hydroxide. Solution in sulphuric acid is red, giving a bluish-black precipitate on dilution.

Literature.—E. P. 6651 of 1899; D. R. P. appl. G. 13069; F. P. 286620; A. P. 636065.

Chicago Orange G (G.). Prepared by condensing *p*-nitrotoluenesulphonic acid with benzidine in presence of sodium hydroxide. Orange-yellow aqueous solution gives a brown precipitate with hydrochloric acid, and an orange-brown one with sodium hydroxide. Solution in sulphuric acid is violet, giving a brown precipitate on dilution.

Literature.—E. P. 788 of 1893; D. R. P. 75326; F. P. 227271.

Arnica Yellow (G.). Prepared by condensing *p*-nitrotoluenesulphonic acid with *p*-aminophenol in presence of boiling aqueous sodium hydroxide. Brownish-yellow aqueous solution gives a brownish-black precipitate with hydrochloric acid. Solution in sulphuric acid is violet, giving a dark-brown precipitate on dilution.

Literature.—F. P. 222554.

Diphenyl Chrysoïne G (G.). Prepared by ethylating the preceding. The constitution is probably

$$\begin{array}{l} CH\cdot C_6H_3(SO_3Na)\cdot N:N\cdot C_6H_4\cdot O\cdot C_2H_5 \\ \| \\ CH\cdot C_6H_3(SO_3Na)\cdot N:N\cdot C_6H_4\cdot O\cdot C_2H_5 \end{array}$$

Golden-yellow aqueous solution gives a blackish brown precipitate with hydrochloric acid, and an orange one with sodium hydroxide. Solution in sulphuric acid is violet-red, giving a blackish-brown precipitate on dilution.

Literature.—E. P. 6651 of 1899; D. R. P. appl. G. 7525, 13069; F. P. 286620; A. P. 636065.

Diphenyl Chrysoïne RR (G.). Prepared by diazotising diphenyl orange RR (G.), combining the diazo- compound with phenol and ethylating the product. Reddish-orange aqueous solution gives a blackish-brown precipitate with hydrochloric acid, and a reddish-brown one with sodium hydroxide. Solution in sulphuric acid is pure blue, giving a brownish-black precipitate on dilution.

Literature.—E. P. 6651 of 1899; D. R. P. 117729; F. P. 286620; A. P. 644462.

Diphenyl Fast Brown G (G.). Prepared as the preceding, but the diazo- compound is combined with 7-phenylamino-*a*-naphthol-3-sulphonic acid. The dark yellowish-brown aqueous solution gives a blackish-brown precipitate with hydrochloric acid, and a dark-brown one with sodium hydroxide. Solution in sulphuric acid is dark blue, giving a blackish-brown precipitate on dilution.

References as above.

Diphenyl Catechine G (G.). Prepared as above, but the diazo- compound is combined with 7-dimethylamino-*a*-naphthol-3-sulphonic acid. Yellowish-brown aqueous solution gives a dark-brown precipitate with hydrochloric acid, and a brown one with sodium hydroxide. Solution in sulphuric acid is blackish violet-blue, giving a blackish-brown precipitate on dilution.

References as above.

Curcuphenine (Cl. Co.). Prepared by condensing *p*-nitrotoluenesulphonic acid with dehydrothio-*p*-toluidinesulphonic acid in presence of very dilute aqueous sodium hydroxide. Yellow aqueous solution gives a brown precipitate with hydrochloric acid. The solution in sulphuric acid is red, giving a brownish-yellow precipitate on dilution.

Literature.—E. P. 12922 of 1896; D. R. P. 99575; F. P. 264755.

Chlorophenine Orange (various marks) (Cl. Co.) are reduction products of the preceding.

IV. TRISAZO- COLOURING MATTERS.

These colours, as their name implies, contain three azo-groups.

Janus Brown B (M.):

$N(CH_3)_3Cl\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot N_2\cdot C_6H_2(NH_2)_2\cdot N_2\cdot C_6H_5$

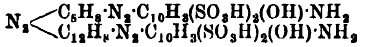
Prepared by combining diazotised *m*-aminophenyltrimethylammonium chloride with *a*-naphthylamine, diazotising the product and combining with chrysoidine. Aqueous solution is brown, giving a soluble brown precipitate with hydrochloric acid or sodium hydroxide. Solution in sulphuric acid is dark green, becoming brown on dilution.

Literature.—E. P. 9343 of 1896; D. R. P. 95530.

Janus Brown R (M.) is prepared from diazotised *p*-aminobenzyldiethylamine and *a*-naphthylamine, the product being diazotised and combined with chrysoidine, resorcinol, or *m*-phenylenediamine. Reactions are similar to those given by the preceding colour.

Literature.—E. P. 19976 of 1896; D. R. P. 99127; F. P. 256156; A. P. 610345; *see* also D. R. P. 93499, 100420; F. P. 264579; A. P. 602638, 602639, 602640, 623697, 626913.

Melogene Blue BH (K. S.); **Diamine Beta Black** (C.)

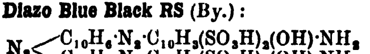


$$N_2\left<\begin{array}{l}C_8H_8\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)\cdot NH_2\\ C_{12}H_8\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)\cdot NH_2\end{array}\right.$$

Tetrazotised benzidine is combined with 1 mol. of *p*-xylidine, the product diazotised and combined with 2 mols. of 8-amino-*a*-naphthol-3 : 6-disulphonic acid (H-acid). The violet-blue aqueous solution gives a violet precipitate with hydrochloric acid, and becomes violet with sodium hydroxide. The solution in sulphuric acid is blue, giving a bluish-violet precipitate on dilution.

Literature.—E. P. 28810 of 1896; F. P. 262109; A. P. 591616.

Diazo Blue Black RS (By.):

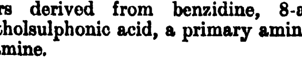


$$N_2\left<\begin{array}{l}C_{10}H_6\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)\cdot NH_2\\ C_{12}H_8\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)\cdot NH_2\end{array}\right.$$

Tetrazotised benzidine is combined with 1 mol. of *a*-naphthylamine, the product diazotised and combined with 2 mols. of H-acid. The dark blue aqueous solution gives a blue precipitate with hydrochloric acid, and becomes redder with sodium hydroxide. The solution in sulphuric acid is dark bluish-green, giving a blue precipitate on dilution.

Direct Black V and **RR** (P.) are analogous colours derived from benzidine, 8-amino-*a*-naphtholsulphonic acid, a primary amine, and a *m*-diamine.

Benzo Gray S extra (By.):

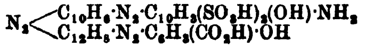


$$N_2\left<\begin{array}{l}C_{10}H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH\\ C_{12}H_8\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH\end{array}\right.$$

The colouring matter from tetrazotised benzidine and 1 mol. each of salicylic acid and *a*-naphthylamine is diazotised and combined with *a*-naphthol-4-sulphonic acid. The Bordeaux-brown aqueous solution gives a black precipitate with hydrochloric acid. The solution in sulphuric acid is blue, giving a black precipitate on dilution.

Literature.—E. P. 13235 of 1890; D. R. P. 57331; F. P. 187365.

Benzo Olive (By.):

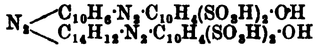


$$N_2\left<\begin{array}{l}C_{10}H_6\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)\cdot NH_2\\ C_{12}H_8\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH\end{array}\right.$$

Prepared as the preceding, except that 8-amino-*a*-naphthol-3 : 6-disulphonic acid (H-acid) is used as the end component. The dark moss-green aqueous solution gives a blackish-grey precipitate with hydrochloric acid, and becomes dark brown with sodium hydroxide. Solution in sulphuric acid is violet, giving a greenish-black precipitate on dilution.

Literature.—E. P. 3439 of 1891; D. R. P. 65480; F. P. 187365.

Congo Fast Blue R (A.); **Benzo Fast Blue R** (By.):

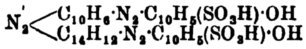


$$N_2\left<\begin{array}{l}C_{10}H_6\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH\\ C_{14}H_{12}\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH\end{array}\right.$$

Tolidine is tetrazotised and combined with 1 mol of *a*-naphthylamine, the product diazotised and combined with 2 mols. of *a*-naphthol-3 : 8-disulphonic acid (*ε*-acid). The blue aqueous solution is precipitated with acids or alkalis. The solution in sulphuric acid is blue, giving a blue precipitate on dilution.

Literature.—E. P. 6932 of 1890; D. R. P. 60921; F. P. 205615.

Benzo Black Blue R (By.):

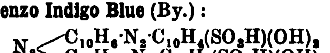


$$N_2\left<\begin{array}{l}C_{10}H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH\\ C_{14}H_{12}\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH\end{array}\right.$$

Tolidine is tetrazotised and combined with 1 mol. of *a*-naphthylamine and the intermediate product diazotised and combined with 2 mols. of *a*-naphthol-4-sulphonic acid. Bluish-violet aqueous solution gives a violet precipitate with hydrochloric acid. Solution in sulphuric acid is blue, giving a bluish-violet precipitate on dilution.

Literature.—E. P. 16484 of 1887; F. P. 187365; A. P. 440639.

Benzo Indigo Blue (By.):

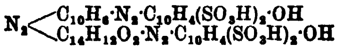


$$N_2\left<\begin{array}{l}C_{10}H_6\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)_2\\ C_{14}H_{12}\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)_2\end{array}\right.$$

The same intermediate tetrazo-compound as above is combined with 2 mols. of 1 : 8-dihydroxynaphthalene-4-sulphonic acid (S-acid). The violet aqueous solution gives a bluish-violet precipitate with hydrochloric acid, and becomes reddish-violet with sodium hydroxide. Solution in sulphuric acid is greenish-blue, giving a violet-blue precipitate on dilution.

Literature.—E. P. 13665 of 1889; D. R. P. 57912; F. P. 200520; A. P. 501118.

Congo Fast Blue B (A.); **Benzo Fast Blue B** (By.):



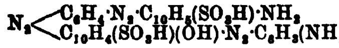
$$N_2\left<\begin{array}{l}C_{10}H_6\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH\\ C_{14}H_{12}O_2\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH\end{array}\right.$$

Dianisidine is tetrazotised and combined with 1 mol. of *a*-naphthylamine and the intermediate product diazotised and combined with 2 mols. of *a*-naphthol-3 : 8-disulphonic acid (*ε*-acid). Blue aqueous solution gives a blue precipitate with acids or alkalis. Solution in sulphuric acid is cornflower blue, giving a blue precipitate on dilution.

Literature.—E. P. 6932 of 1890; D. R. P. 57444; F. P. 205615.

Columbia Black FB and **FF extra** (A.); **Azidine Black FF** (C. J.); **Titan Blacks** (H.);

Dianol Black FB. FF (Lev.); **Panama Black R, F** (Sch.); **Patent Dianil Black FF extra** (M.):



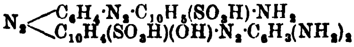
$$N_2 \Big\langle \begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \\ C_{10}H_4(SO_3H)(OH){\cdot}N_2{\cdot}C_6H_3(NH_2)_2 \end{array}$$

p-Aminoacetanilide is diazotised and combined with 7-amino-α-naphthol-3-sulphonic acid (γ-acid), the product saponified with sodium hydroxide, the resulting diamino-compound tetrazotised and combined first with 1 mol. of α-naphthylamine-6- (or 7)-sulphonic acid (Cleve's acids) and then with 1 mol. of *m*-phenylenediamine. The aqueous solution is violet-black, and is precipitated by acids or alkalis. Solution in sulphuric acid is blue, giving a precipitate on dilution.

Literature.—E. P. 12804 of 1900; D. R. P. 131986, 131987; F. P. 302499; A. P. 679221.

Direct Black BMP (P.) has the same or a very similar constitution, and dyestuffs belonging to the same class are **Carbon Blacks** (various marks) (K.), and **Naphthamine Direct Blacks FF, B, FG** and **CS** (K.). They are of the type described in D. R. P. 126671, viz. *p*-nitroaniline-*o*-sulphonic acid is diazotised and combined with Cleve's acids, the product reduced, tetrazotised and combined with 2 mols. of a meta-diamine.

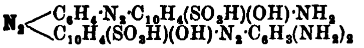
Titan Black J (H.):



$$N_2 \Big\langle \begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}NH_2 \\ C_{10}H_4(SO_3H)(OH){\cdot}N_2{\cdot}C_6H_3(NH_2)_2 \end{array}$$

p-Aminoacetanilide is diazotised and combined with 6-amino-α-naphthol-3-sulphonic acid (J-acid), the product saponified, tetrazotised, and combined with 1 mol. each of α-naphthylamine-6-(or 7)-sulphonic acid (Cleve's acids) and *m*-phenylenediamine.

Oxydiamine Black N (C.):

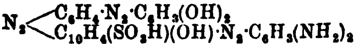


$$N_2 \Big\langle \begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2 \\ C_{10}H_4(SO_3H)(OH){\cdot}N_2{\cdot}C_6H_3(NH_2)_2 \end{array}$$

Prepared like Columbia black FB, except that 7-amino-α-naphthol-3-sulphonic acid (γ-acid) is used instead of Cleve's acid. Blue-black aqueous solution gives a black-violet precipitate with hydrochloric acid, and a red-violet one with sodium hydroxide. Solution in sulphuric acid is greenish-blue, giving a violet-black precipitate on dilution.

Literature.—A. P. 526763.

Isodiphenyl Black R (G.):

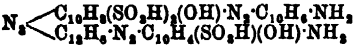


$$N_2 \Big\langle \begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_6H_3(OH)_2 \\ C_{10}H_4(SO_3H)(OH){\cdot}N_2{\cdot}C_6H_3(NH_2)_2 \end{array}$$

Prepared as Columbia black FB, except that resorcinol is used instead of Cleve's acid. Violet-black aqueous solution gives a black precipitate with acids or alkalis. Solution in sulphuric acid is blackish-blue, giving a black precipitate on dilution.

Literature.—E. P. 20278 of 1897; F. P. 270151; A. P. 615497.

Direct Black V (K. S.); **Diazo Direct Black** (Wiescher & Co.):

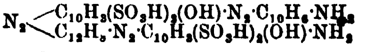


$$N_2 \Big\langle \begin{array}{l} C_{10}H_3(SO_3H)_2(OH){\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2 \\ C_{12}H_8{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2 \end{array}$$

7-Amino-α-naphthol-3 : 6-disulphonic acid (2 R-acid) is diazotised and combined with 1 mol. of α-naphthylamine in acid solution. The mono-azo-dyestuff is then dissolved by adding sodium hydroxide and tetrazotised benzidine added, the combination being effected in presence of sodium carbonate. To this intermediate product is then added 1 mol. of 7-amino-α-naphthol-3-sulphonic acid (γ-acid). Violet-black aqueous solution gives a blue-black precipitate with hydrochloric acid, and becomes reddish-violet with sodium hydroxide. Solution in sulphuric acid is blue, giving a blue-black precipitate on dilution.

Literature.—E. P. 15294 of 1896; D. R. P. 109161; F. P. 256950; A. P. 601033.

Direct Indone Blue R (K. S.):

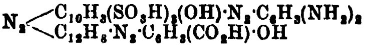


$$N_2 \Big\langle \begin{array}{l} C_{10}H_3(SO_3H)_2(OH){\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2 \\ C_{12}H_8{\cdot}N_2{\cdot}C_{10}H_3(SO_3H)_2(OH){\cdot}NH_2 \end{array}$$

Prepared as the preceding, except that 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid) is used as the end-component. Blue-black aqueous solution gives a dark-blue precipitate with hydrochloric acid, and becomes violet with sodium hydroxide. Solution in sulphuric acid is blue, giving a dark-blue precipitate on dilution.

References as above.

Diamine Bronze G (C.):



$$N_2 \Big\langle \begin{array}{l} C_{10}H_3(SO_3H)_2(OH){\cdot}N_2{\cdot}C_6H_3(NH_2)_2 \\ C_{12}H_8{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH \end{array}$$

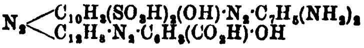
The dyestuff from tetrazotised benzidine and 1 mol. each of salicylic acid and 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid) is diazotised and combined with 1 mol. of *m*-phenylenediamine. The chocolate-brown aqueous solution gives a purple-brown precipitate with hydrochloric acid, and becomes yellower with sodium hydroxide. Solution in sulphuric acid is bluish-violet, giving a black precipitate on dilution.

Literature.—E. P. 6972 of 1891; D. R. P. 75762; F. P. 201770.

Trisulphone Browns B, G and **GG** (K. S.). These are constituted similarly to the preceding, except that 7-amino-α-naphthol-3 : 6-disulphonic acid (2 R-acid) is employed instead of H-acid. The diamines used are benzidine (for **B**), tolidine (for **G**), and dianisidine (for **GG**). Each brand gives a brown solution in water, which yields a blackish-brown precipitate with hydrochloric acid, and becomes red with sodium hydroxide. The solution in sulphuric acid is bluish-violet, giving a dark-brown precipitate on dilution.

Literature.—E. P. 5746 of 1898; D. R. P. 114638; F. P. 275733; A. P. 608024.

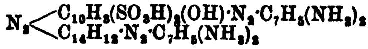
Chlorazol Deep Brown B (H.):



$$N_2 \Big\langle \begin{array}{l} C_{10}H_3(SO_3H)_2(OH){\cdot}N_2{\cdot}C_7H_5(NH_2)_2 \\ C_{12}H_8{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH \end{array}$$

Benzidine is tetrazotised and combined with 1 mol. each of salicylic acid and 7-amino-α-naphthol-3 : 6-disulphonic acid (2 R-acid), the product being diazotised and combined with *m*-tolylenediamine.

Columbia Black R (A.):



$$N_2 \Big\langle \begin{array}{l} C_{10}H_3(SO_3H)_2(OH){\cdot}N_2{\cdot}C_7H_5(NH_2)_2 \\ C_{14}H_{12}{\cdot}N_2{\cdot}C_7H_5(NH_2)_2 \end{array}$$

Tolidine is tetrazotised and combined with 1 mol. each of 7-amino-α-naphthol-3 : 6-disulphonic acid (2 R-acid and *m*-tolylenediamine, and the product is diazotised and combined with *m*-tolylenediamine. Brown-black aqueous solution gives a black precipitate with hydrochloric acid, and becomes brown with sodium hydroxide. Solution in sulphuric acid is pure blue, giving a violet-black precipitate on dilution.

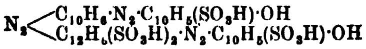
Literature.—E. P. 14895 of 1893; D. R. P. 102815; F. P. 231976.

Columbia Black B (A.); **Titan Black M** (H.); **Direct Blue Black B, 2 B** (By.). Prepared as the preceding, except that dianisidine is used instead of benzidine. The violet-black aqueous solution gives a dark flocculent precipitate with hydrochloric acid, and becomes reddish-violet with sodium hydroxide. Solution in sulphuric acid is blue-black, giving a violet-black precipitate on dilution.

Literature.—E. P. 14895 of 1893; D. R. P. 111744; F. P. 231976.

Columbia Blacks 2 BX and **2 BW** (A.) belong to the same class.

Benzo Black Blue G (By.):



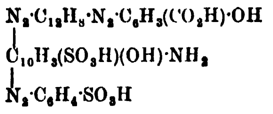
$$N_2\begin{cases} C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH \\ C_{12}H_6(SO_3H)_2{\cdot}N_2{\cdot}C_{10}H_5(SO_3H){\cdot}OH \end{cases}$$

Benzidinedisulphonic acid is tetrazotised and combined with 1 mol. of *a*-naphthylamine, the product diazotised and combined with 2 mols. of *a*-naphthol-4-sulphonic acid. The blue-black aqueous solution gives a black-blue precipitate with hydrochloric acid, and becomes blue with sodium hydroxide. The solution in sulphuric acid is blackish-green, giving a blackish-blue precipitate on dilution.

Literature.—E. P. 16484 of 1887; D. R. P. 44779; Ber. 1889, 22, 3463.

Benzo Black Blue 5 G (By.). As the preceding, except that 1 : 8-dihydroxynaphthalene-4-sulphonic acid is used instead of *a*-naphthol-4-sulphonic acid. The blackish-blue aqueous solution gives a dark greenish-blue precipitate with hydrochloric acid. The solution in sulphuric acid is black-green, giving a dark greenish-blue precipitate on dilution.

Columbia Green (A.); **Direct Green CO** (L.):

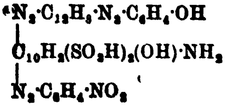


$$\begin{array}{l} N_2{\cdot}C_{12}H_8{\cdot}N_2{\cdot}C_6H_3(CO_2H){\cdot}OH \\ | \\ C_{10}H_3(SO_3H)(OH){\cdot}NH_2 \\ | \\ N_2{\cdot}C_6H_4{\cdot}SO_3H \end{array}$$

Benzidine is tetrazotised and combined with 1 mol. of salicylic acid, and the intermediate product is combined in alkaline solution with the product of the action of diazotised sulphanilic acid on 8-amino-*a*-naphthol-5-sulphonic acid (S-acid) in acid solution. The green aqueous solution gives a green precipitate with hydrochloric acid, and becomes greenish-black with sodium hydroxide. The solution in sulphuric acid is blue-violet, giving a green precipitate on dilution. When diazotised aniline is used instead of diazotised sulphanilic acid in the above, **Columbia Black Green D** (A.) is produced.

Literature.—D. R. P. appl. A. 3574.

Diamine Green B (C.); **Dianol Green B** (Lev.); **Renol Green B** (T. M.); **Direct Green BN** (P.); **Azidine Green 2 B** (C. J.); **Dianil Green B** (M.); **Alkali Green** (D.); **Oxamine Green B** (B.):



$$\begin{array}{l} N_2{\cdot}C_{12}H_8{\cdot}N_2{\cdot}C_6H_4{\cdot}OH \\ | \\ C_{10}H_2(SO_3H)_2(OH){\cdot}NH_2 \\ | \\ N_2{\cdot}C_6H_4{\cdot}NO_2 \end{array}$$

Prepared in a similar manner as the preceding. Tetrazotised benzidine is combined with 1 mol. of phenol and the product is combined with the azo-colour from diazotised *p*-nitroaniline and 8-amino-*a*-naphthol-3 : 6-disulphonic acid (H-acid). Dull-green aqueous solution gives a bluish-black precipitate with hydrochloric acid, and becomes yellower with sodium hydroxide. Solution in sulphuric acid is violet, giving a black precipitate on dilution.

Literature.—E. P. 15725 of 1891; D. R. P. 66351; F. P. 201770; A. P. 514599.

Diamine Green G (C.); **Chlorazol Green G** (H.); **Dianol Green G** (Lev.); **Azidine Green 2 G** (C. J.); **Alkali Green D** (D.); **Dianil Green BBN, G** (M.); **Benzoin Dark Green** (B. K.); **Erie Direct Green MT, BT** (Sch.); **Oxamine Green G** (B.). Prepared as the preceding, except that salicylic acid is used instead of phenol.

Reactions and literature as above.

Eboli Green (various marks) (L.). Tetrazotised benzidine combined with 1 mol. of salicylic acid is combined with the product of the action of diazotised sulphanilic acid on 8-amino-*a*-naphthol-4 : 6-disulphonic acid.

Literature.—E. P. 19253 of 1895; D. R. P. appl. F. 8626; A. P. 606439.

Diphenyl Green G (G.). Prepared like diamine green B (above), except that *o*-chloro-*p*-nitroaniline is used instead of *p*-nitroaniline. The reactions are also similar to those given by this colour.

Literature.—A. P. 628233.

Diphenyl Green 3 G (G.). Prepared like diamine green G, *o*-chloro-*p*-nitroaniline being used instead of *p*-nitroaniline. The green aqueous solution gives a green precipitate with hydrochloric acid, and becomes duller with sodium hydroxide. Solution in sulphuric acid is reddish-violet, giving a green precipitate on dilution.

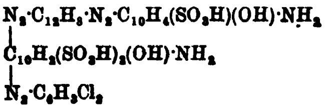
Reference as the preceding.

Chloramine Green B (K. S.). Prepared like diamine green B, 2 : 5-dichloroaniline being used instead of *p*-nitroaniline. The green aqueous solution gives a violet-black precipitate with hydrochloric acid, and becomes black-green with sodium hydroxide. Solution in sulphuric acid is violet, giving a violet-black precipitate on dilution.

Literature.—E. P. 8503 of 1899; D. R. P. 112820; F. P. 287971; A. P. 627679.

Chloramine Black N (K. S.). Tetrazotised benzidine is combined with 1 mol. of *m*-phenylenediamine and the product combined with the azo-colour from diazotised 2 : 5-dichloroaniline and H-acid. The dark bluish-green aqueous solution gives a blue precipitate with hydrochloric acid, and a bluish-green precipitate with sodium hydroxide. Solution in sulphuric acid is blue, giving a blue precipitate on dilution.

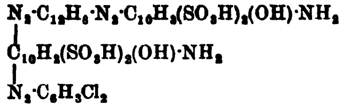
Chloramine Blue HW (K. S.):



$$\begin{array}{l} N_2{\cdot}C_{12}H_8{\cdot}N_2{\cdot}C_{10}H_4(SO_3H)(OH){\cdot}NH_2 \\ | \\ C_{10}H_2(SO_3H)_2(OH){\cdot}NH_2 \\ | \\ N_2{\cdot}C_6H_3Cl_2 \end{array}$$

Tetrazotised benzidine is combined with 1 mol. of *γ*-acid in alkaline solution and then, also in alkaline solution, with the product of the action of diazotised 2 : 5-dichloroaniline on H-acid (1 mol.) in acid solution.

Chloramine Blue 3 G (K. S.):

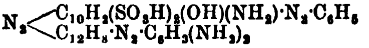


$$N_2\cdot C_{12}H_8\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)\cdot NH_2 \,|\, C_{10}H_2(SO_3H)_2(OH)\cdot NH_2 \,|\, N_2\cdot C_6H_3Cl_2$$

Tetrazotised benzidine is combined with 1 mol. of 8-amino-α-naphthol-3 : 6-disulphonic acid (H-acid) and then with 1 mol. of H-acid to which has been added 1 mol. of diazotised dichloroaniline in acid solution.

References for the last two colours as for chloramine green B.

Erie Direct Black GX (Sch.); **Renol Black G** (T. M.); **Patent Dianil Black EB** (M.); **Union Black** (By.); **Direct Deep Black EW** (By.); **Cotton Black RW** (B.):

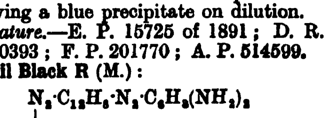


$$N_2<\begin{matrix}C_{10}H_2(SO_3H)_2(OH)(NH_2)\cdot N_2\cdot C_6H_5\\ C_{12}H_8\cdot N_2\cdot C_6H_3(NH_2)_2\end{matrix}$$

Tetrazotised benzidine is combined with 1 mol· of H-acid in acid solution, after making alkaline 1 mol. of diazotised aniline is added, and then 1 mol. of *m*-phenylenediamine. When *m*-tolylenediamine is used in the last combination the colour is known as **Erie Direct Black RX** (Sch.); **Renol Black R** (T. M.); **Patent Dianil Black EBV** (M.); **Direct Deep Black RW** (By.); **Cotton Black E** (B.). The aqueous solutions of both dyes become violet with hydrochloric acid and blue with sodium hydroxide and the sulphuric acid solutions are violet blue. With phenol as end component **Erie Direct Green ET** (Sch.) is obtained. The green aqueous solution becomes blue with hydrochloric acid and greenish black with sodium hydroxide. The solution in sulphuric acid is bluish-green, becoming blue on dilution.

Literature.—E. P. 12305 of 1902; D. R. P. 153557 and appl. A. 8974; F. P. 321626; A. P. 688478, 717550.

Diamine Black HW (C.); **Ingrain Black G** (H.); **Naphthamine Black H** (K.):

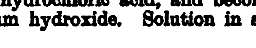


$$N_2\cdot C_{12}H_8\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2 \,|\, C_{10}H_2(SO_3H)_2(OH)\cdot NH_2 \,|\, N_2\cdot C_6H_4\cdot NO_2$$

Prepared like diamine green B (above), except that 7-amino-α-naphthol-3-sulphonic acid (γ-acid) is used instead of phenol. Blackish-blue aqueous solution gives a blue precipitate with hydrochloric acid. Solution in sulphuric acid is blue, giving a blue precipitate on dilution.

Literature.—E. P. 15725 of 1891; D. R. P. 66351, 70393; F. P. 201770; A. P. 514599.

Dianil Black R (M.):

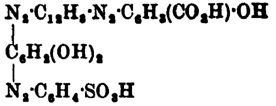


$$N_2\cdot C_{12}H_8\cdot N_2\cdot C_6H_3(NH_2)_2 \,|\, C_{10}H_3(SO_3H)_2(OH)_2 \,|\, N_2\cdot C_{10}H_6\cdot SO_3H$$

Tetrazotised benzidine is combined with 1 mol. of *m*-phenylenediamine and then with 1 mol. of 1 : 8 - dihydroxynaphthalene-3 : 6 - disulphonic acid (chromotrope acid), to which has been added 1 mol. of diazotised naphthionic acid. The reddish-violet aqueous solution gives a precipitate with hydrochloric acid, and becomes blue with sodium hydroxide. Solution in sulphuric acid is dark blue, giving a reddish-violet precipitate on dilution.

Literature.—D. R. P. 89285.

Congo Brown G (A.) (Lev.); **Naphthamine Brown 4 G** (K.); **Benzoin Brown C** (B. K.); **Direct Brown GR** (Sch.):

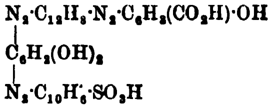


$$N_2\cdot C_{12}H_8\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH \,|\, C_6H_2(OH)_2 \,|\, N_2\cdot C_6H_4\cdot SO_3H$$

The dyestuff from tetrazotised benzidine, salicylic acid and resorcinol is treated with diazotised sulphanilic acid or the intermediate product from tetrazotised benzidine and 1 mol. of salicylic acid is combined with 1 mol. of resorcinol to which 1 mol. of diazotised sulphanilic acid has been added. The red aqueous solution gives a brown precipitate with hydrochloric acid. Solution in sulphuric acid is reddish-violet, giving a reddish-brown precipitate on dilution.

Literature.—E. P. 10653 of 1888; D. R. P. 46328, 46501; F. P. 192331; A. P. 399581.

Congo Brown R (A.) (Lev.):

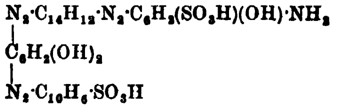


$$N_2\cdot C_{12}H_8\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH \,|\, C_6H_2(OH)_2 \,|\, N_2\cdot C_{10}H_6\cdot SO_3H$$

Prepared as the preceding, except that α-naphthylamine-5-sulphonic acid (Laurent's acid) is used instead of sulphanilic acid. Reactions and references as the preceding.

Benzamine Brown 3 GO (D.) is prepared as Congo brown G, except that *m*-phenylenediamine is used instead of resorcinol. The reddish-yellow aqueous solution gives a brown precipitate with hydrochloric acid, and becomes brownish-yellow with sodium hydroxide. Solution in sulphuric acid is brownish-violet, giving a brown precipitate on dilution.

Azo Corinth (O.):



$$N_2\cdot C_{14}H_{12}\cdot N_2\cdot C_6H_2(SO_3H)(OH)\cdot NH_2 \,|\, C_6H_2(OH)_2 \,|\, N_2\cdot C_{10}H_6\cdot SO_3H$$

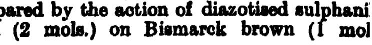
Tetrazotised tolidine is combined with 1 mol. of 3-aminophenol-6-sulphonic acid (acid III.) and 1 mol. of resorcinol, and the colouring matter so obtained is treated with 1 mol. of diazotised naphthionic acid. Reddish-brown aqueous solution gives a reddish-brown precipitate with hydrochloric acid, and is turned bluish-red with sodium hydroxide. Solution in sulphuric acid is bluish-violet, giving a reddish-brown precipitate on dilution.

Literature.—E. P. 13402 of 1893; D. R. P. 71182; A. P. 516381.

V. TETRAKISAZO- COLOURING MATTERS.

These contain four azo-groups.

Benzo Brown G (By.) (Marden, Orth and Hastings Corporation):



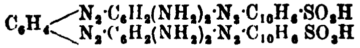
$$C_6H_4<\begin{matrix}N_2\cdot C_6H_2(NH_2)_2\cdot N_2\cdot C_6H_4\cdot SO_3H\\ N_2\cdot C_6H_2(NH_2)_2\cdot N_2\cdot C_6H_4\cdot SO_3H\end{matrix}$$

Prepared by the action of diazotised sulphanilic acid (2 mols.) on Bismarck brown (1 mol

Reddish-brown aqueous solution gives a brown precipitate with acids and alkalis. Solution in sulphuric acid is violet-brown, giving a brown precipitate on dilution.

Literature.—E. P. 16493 of 1887; D. R. P. 46804; A. P. 384315.

Benzo Brown B (By.):



$$\mathrm{C_6H_4}\left<\begin{array}{l}\mathrm{N_2\cdot C_6H_2(NH_2)_2\cdot N_2\cdot C_{10}H_6\cdot SO_3H}\\ \mathrm{N_2\cdot C_6H_2(NH_2)_2\cdot N_2\cdot C_{10}H_6\,SO_3H}\end{array}\right.$$

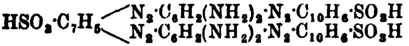
Prepared as the preceding, except that naphthionic acid is used instead of sulphanilic acid.

Reactions and references as above.

Direct Brown J (I.). Prepared as benzo brown G, except that aminobenzoic acid is used instead of sulphanilic acid. The yellowish brown aqueous solution gives a dark brown precipitate with hydrochloric acid. Solution in sulphuric acid is brown, giving a brown precipitate on dilution.

Literature.—D. R. P. 76127; F. P. 219925; A. P. 491422.

Toluylene Brown R (O.); **Azidine Brown T 2 R** (C. J.); **Direct Brown R** (Sch.):

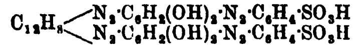


$$\mathrm{HSO_3\cdot C_7H_5}\left<\begin{array}{l}\mathrm{N_2\cdot C_6H_2(NH_2)_2\cdot N_2\cdot C_{10}H_6\cdot SO_3H}\\ \mathrm{N_2\cdot C_6H_2(NH_2)_2\cdot N_2\cdot C_{10}H_6\cdot SO_3H}\end{array}\right.$$

Prepared by treating the colour from tetrazotised 2 : 6-tolylenediamine-4-sulphonic acid and 2 mols. of *m*-phenylenediamine with 2 mols. of diazotised naphthionic acid. Brown aqueous solution gives a brown precipitate with hydrochloric acid. Solution in sulphuric acid is dull reddish-violet.

Literature.—E. P. 11000 of 1889; D. R. P. 58657; F. P. 199658; A. P. 465116.

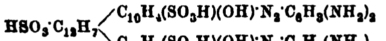
Hessian Brown BBN (L.):



$$\mathrm{C_{12}H_8}\left<\begin{array}{l}\mathrm{N_2\cdot C_6H_2(OH)_2\cdot N_2\cdot C_6H_4\cdot SO_3H}\\ \mathrm{N_2\cdot C_6H_2(OH)_2\cdot N_2\cdot C_6H_4\cdot SO_3H}\end{array}\right.$$

Prepared by the action of tetrazotised benzidine on 2 mols. of the monoazo-dyestuff from diazotised sulphanilic acid and resorcinol. Aqueous solution is brown, giving a brown precipitate with hydrochloric acid, and becoming red with sodium hydroxide. Solution in sulphuric acid is violet-black, giving a brown precipitate on dilution.

Dianil Black PR (M.):

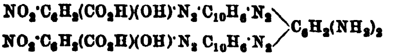


$$\mathrm{HSO_3\cdot C_{12}H_7}\left<\begin{array}{l}\mathrm{C_{10}H_4(SO_3H)(OH)\cdot N_2\cdot C_6H_3(NH_2)_2}\\ \mathrm{C_{10}H_4(SO_3H)(OH)\cdot N_2\cdot C_6H_3(NH_2)_2}\end{array}\right.$$

Benzidinesulphonic acid is tetrazotised and combined with 2 mols. of 7-amino-α-naphthol-3-sulphonic acid (γ-acid) in alkaline solution, and the product is tetrazotised and combined with 2 mols. of *m*-phenylenediamine. Black aqueous solution is precipitated with hydrochloric acid or sodium hydroxide. Solution in sulphuric acid is dark-blue, giving a black precipitate on dilution.

Literature.—E. P. 13743 of 1896; F. P. 257245; A. P. 578530.

Anthracene Acid Brown B (C.):



$$\left.\begin{array}{l}\mathrm{NO_2\cdot C_6H_2(CO_2H)(OH)\cdot N_2\cdot C_{10}H_6\cdot N_2}\\ \mathrm{NO_2\cdot C_6H_2(CO_2H)(OH)\cdot N_2\,C_{10}H_6\cdot N_2}\end{array}\right>\mathrm{C_6H_2(NH_2)_2}$$

Nitroaminosalicyclic acid is diazotised and combined with α-naphthylamine. Two mols. of this are diazotised and combined with 1 mol. of *m*-phenylenediamine. Brown aqueous solution gives a violet precipitate with hydrochloric acid. Solution in sulphuric acid is greyish-violet, giving a brown-violet precipitate on dilution.

Literature.—E. P. 2446 of 1896; D. R. P. 92655; F. P. 253834.

J. C. C.

AZO- ACID YELLOW, -ALIZARIN YELLOW, -BLACK BASE O, -BORDEAUX, -CHROMINE, -COCCINE, -COCHINEAL, -CORALLINE, -EOSINE, -FLAVINE, -FUCHSINES, -VIOLET (*v.* Azo- colouring matters.

AZODERMIN. Acetylamidoazotoluene.

AZOERYTHRIN *v.* Archil.

AZOFLAVIN *v.* Azo- colouring matters.

AZOGEN RED *v.* Azo- colouring matters.

AZOGRENADINES *v.* Azo- colouring matters.

AZOIMIDE (*Hydrazoic acid*) N_3H was first isolated in 1890 by Curtius (Ber. 1890, 23, 3023), although in the form of its phenyl derivative (diazobenzeneimide) $C_6H_5N_3$ it was known in 1866, having been then prepared by P. Griess (Annalen, 1866, 137, 65, 77).

Curtius obtained azoimide by the action of sodium nitrite and acetic acid on benzoyl hydrazine, the nitroso- derivative first formed passing into benzoyl azoimide by loss of water

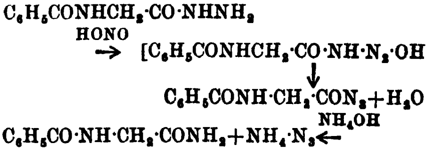
$$\mathrm{C_6H_5CO\cdot NH\cdot NH_2+HONO=}$$
$$\mathrm{H_2O+C_6H_5CO\cdot N(NO)\cdot NH_2\rightarrow H_2O+C_6H_5CON_3}$$

The benzoyl azide so obtained was dissolved in an equal weight of absolute alcohol and digested on the water-bath with 1 mol. proportion of sodium, also dissolved in absolute alcohol, when sodium azide was formed, and this was precipitated from the solution by the addition of ether:

$$\mathrm{C_6H_5CON_3+2NaOH}$$
$$\mathrm{=H_2O+C_6H_5COONa+NaN_3}$$

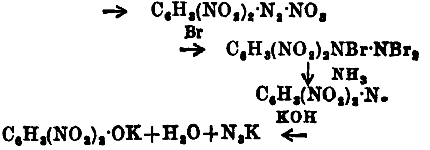
The following methods have also been employed for the preparation of azoimide and its salts.

1. Hippuryl hydrazine by the action of nitrous acid is converted into hippurazide, from which by the action of ammonia, ammonium azide is produced (Curtius, Ber. 1891, 24, 3341):



$$\begin{array}{l}\mathrm{C_6H_5CONHCH_2\cdot CO\cdot NHNH_2}\\ \qquad\xrightarrow{\mathrm{HONO}}\ \mathrm{[C_6H_5CONHCH_2\cdot CO\cdot NH\cdot N_2\cdot OH}\\ \qquad\qquad\qquad\qquad\qquad\downarrow\\ \qquad\qquad\qquad\mathrm{C_6H_5CONH\cdot CH_2\cdot CON_3+H_2O}\\ \mathrm{C_6H_5CO\cdot NH\cdot CH_2\cdot CONH_2+NH_4\cdot N_3}\xleftarrow{\mathrm{NH_4OH}}\end{array}$$

2. *o.p*-Diazobenzeneimide (prepared from *o.p*-Dinitro-aniline), on treatment with alcoholic potash, yields potassium azide (Nölting and Grandmougin, Ber. 1892, 25, 3328):



$$\begin{array}{l}o.p.\ \mathrm{C_6H_3(NO_2)_2\cdot NH_2\cdot HNO_3}\\ \qquad\xrightarrow{\mathrm{HONO}}\ \mathrm{C_6H_3(NO_2)_2\cdot N_2\cdot NO_3}\\ \qquad\qquad\qquad\xrightarrow{\mathrm{Br}}\ \mathrm{C_6H_3(NO_2)_2NBr\cdot NBr_2}\\ \qquad\qquad\qquad\qquad\qquad\downarrow\mathrm{NH_3}\\ \qquad\qquad\qquad\qquad\mathrm{C_6H_3(NO_2)_2\cdot N.}\\ \mathrm{C_6H_3(NO_2)_2\cdot OK+H_2O+N_3K}\ \xleftarrow{\mathrm{KOH}}\end{array}$$

3. The decomposition of diazotised amidoguanidine nitrate by caustic alkalis (Thiele. Annalen, 1892, 270, 1):

$$\begin{array}{l}\mathrm{HN:C(NH_2)\cdot NH\cdot NH_2\cdot HNO_3}\\ \qquad\qquad\xrightarrow{\mathrm{HONO}}\ \mathrm{HN:C(NH_2)\cdot NH\cdot N_2\cdot NO_3}\\ \qquad\qquad\rightarrow\quad\mathrm{CN\cdot NH_2+HNO_3+N_3H}\end{array}$$

4. The action of nitrous oxide on sodamide (W. Wislicenus, Ber. 1892, 25, 2084):

$$NaNH_2+N_2O=NaN_3+N_2O$$

5. The action of an aqueous solution of hydrazine on a benzene solution of nitrogen chloride (Tanatar, Ber. 1899, 32, 1399):

$$N_2H_4+NCl_3=N_3H+3HCl$$

6. The oxidation of a mixture of hydrazine sulphate and hydroxylamine hydrochloride by chromic acid mixture (Brown, Ber. 1905, 38, 1825).

7. The decomposition of hydrazine sulphate by potassium nitrite (Dennstedt, Chem. Zeit. 1897, 21, 876):

$$N_2H_4+HONO \rightarrow [NH_2{\cdot}N_2{\cdot}OH] \rightarrow H_2O+N_3H$$

8. The decomposition of hydrazine sulphate by a saturated aqueous solution of silver nitrite, crystalline silver azide being precipitated (Angeli, Ber. 1893, 26, 885, Ref.).

9. In nearly quantitative yield, the sodium salt may be prepared by mixing hydrazine hydrate with sodium methoxide, and adding an ether solution of ethyl nitrite to the mixture. If the free acid be required it is sufficient to shake hydrazine sulphate for several hours with sodium hydroxide solution and ethyl nitrite, about 80–84 p.c. of the hydrazine compound undergoing decomposition (Thiele, Ber. 1908, 41, 2681).

The free acid may be obtained by distilling the salts with dilute sulphuric acid. In the anhydrous condition it is a colourless mobile liquid of very unpleasant odour. It boils at 37° C., and is readily soluble in water. Azoimide is a most dangerous substance to handle on account of the fact that it decomposes with explosive violence on agitation. It somewhat resembles the halogen acids in that it forms difficultly soluble lead, silver and mercurous salts. It is very poisonous, its vapour attacks the mucous membrane rapidly, whilst the aqueous solution of the acid attacks the skin. The metallic salts of the acid all crystallise in the anhydrous state, and when heated, decompose, generally with explosive violence, leaving a residue of the pure metal.

Azoimide is a 'weak' acid, comparable in strength with acetic acid (West, Trans. 1900, 77, 705). The heat of formation of the acid has been measured by Berthelot and Matignon (Compt. rend., 1891, 113, 672), with the following result:

$$3N+H+aq=N_3Haq-61{,}600 \text{ cal.}$$

A 7 p.c. solution of the acid dissolves magnesium and zinc, with evolution of hydrogen. From solutions of ferric, aluminium, chromic and thallium salts the corresponding hydroxides are quantitatively precipitated on boiling with azoimide. On reduction with sodium amalgam, or by zinc and acid, azoimide is converted into ammonia and hydrazine; if, however, sodium sulphide or ferrous hydroxide be used as reducing agents, little hydrazine is formed.

The reaction $N_3H+HNO_2=N_2+N_2O+H_2O$ is quantitative, and can be used for the estimation of simple nitrites. In this method a known excess of sodium azide is added to the acid solution of the nitrite, and the mixture well shaken. The solution is made just alkaline by baryta water, boiled to expel nitrous oxide, acidified by acetic acid and the excess azoimide estimated by titration with iodine and sodium thiosulphate.

Hydrazine azide N_5H_5; is obtained by the action of lead azide on hydrazine sulphate. It crystallises in prisms and is very volatile. When rapidly heated it explodes with great violence.

Iodine azide N_3I is obtained as an unstable nearly colourless solid when silver azide is suspended in water and shaken with a solution of iodine in ether at 0° C. (Hantzsch, Ber. 1900, 33, 522). It decomposes readily, alkaline hydroxides converting it into the corresponding alkali azide $N_3I+2KHO=N_3K+H_2O+KIO$. The aqueous solution of the azide gradually decomposes on keeping $N_3I+H_2O=N_3H+HIO$.

Chlorine azide N_3Cl was prepared in 1908 by Raschig (Ber. 1908, 41, 4194), on adding sodium hypochlorite to sodium azide and acidifying the mixture. It is a colourless gas.

Phenyl azide (Diazobenzene imide) $C_6H_5N_3$ was first prepared by Griess (Annalen, 1866, 137, 65, 77) by decomposing diazobenzene perbromide with ammonia. It is a pale yellow oil boiling at 65·5°–66·5° C., and is volatile in steam. On heating with hydrochloric acid it yields *o*- and *p*-chloroaniline and nitrogen. Reduction in acid solution converts it into aniline and ammonia.

Benzyl azide $C_7H_7N_3$ is obtained as an aromatic smelling oil, by the action of warm acid on nitrosobenzylhydrazine, or by decomposing silver azide with benzyl iodide. It boils at 74° C. (11 mm.).

Azides of the above type may be obtained generally by the following methods:—

1. The decomposition of diazobenzene perbromides with aqueous ammonia:

$$C_6H_5NBr{\cdot}NBr_2+4NH_3=C_6H_5N_3+3NH_4Br$$

2. The decomposition of diazonium sulphates with hydroxylamine:

$$C_6H_5N_2\,HSO_4+NH_2OH=H_2SO_4+H_2O+C_6H_5N_3$$

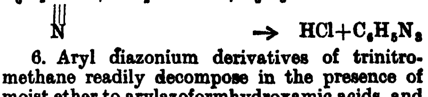
3. The action of nitrous acid on phenyl hydrazine hydrochloride:

$$C_6H_5NH{\cdot}NH_2 \rightarrow C_6H_5N(NO){\cdot}NH_2 \rightarrow H_2O+C_6H_5N_3$$

4. The decomposition of β-phenylsemicarbazides with sodium hypochlorite:

$$C_6H_5NH{\cdot}NH{\cdot}CONH_2 \rightarrow C_6H_5N:N{\cdot}CONH_2 \rightarrow C_6H_5N:N{\cdot}NH_2 \rightarrow C_6H_5N_3$$

5. The action of chloroamine on diazonium salts (M. O. Forster):

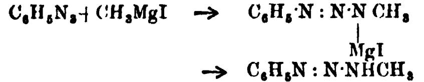


$$\begin{array}{l}C_6H_2{\cdot}\underset{\overset{|||}{N}}{N}{\cdot}Cl+NH_2Cl=HCl+C_6H_5N:N{\cdot}NHCl \\ \qquad\qquad\qquad\qquad \rightarrow HCl+C_6H_5N_3\end{array}$$

6. Aryl diazonium derivatives of trinitromethane readily decompose in the presence of moist ether to arylazoformhydroxamic acids, and the latter on heating with aqueous alkali hydroxides are converted into the corresponding azide (Ponzio, Gazz. 1915, 45, ii. 12; 1916, 46, ii. 56):

$$\begin{array}{lcl}ArN_2O{\cdot}ON:C(NO_2)_2 & \rightarrow & ArN:N{\cdot}CO{\cdot}NHOH \\ & & \quad\downarrow \\ & & ArN_3+CO_2+H_2\end{array}$$

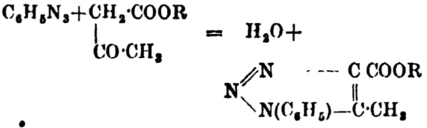
The aryl azides are decomposed on heating with hydrochloric acid, nitrogen being evolved and the corresponding chloro-anilines formed Similarly with sulphuric acid they yield aminophenols. Hot alcoholic potash converts the *o*- and *p*-nitro derivatives into azoimide and the nitrophenols. On condensation with the Grignard reagent and subsequent decomposition diazoamines (triazens) are formed (Dimroth):



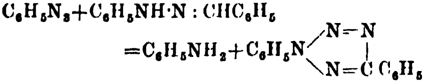
$$C_6H_5N_3+CH_3MgI \rightarrow C_6H_5\cdot N:N\cdot \underset{\textstyle MgI}{\underset{|}{N}}CH_3 \rightarrow C_6H_5N:N\cdot NHCH_3$$

Phenyl methyl triazen

Condensation with β-ketonic esters converts them into triazoles (Ber. 1902, 35, 4041):



whilst with benzaldehyde arylhydrazones they similarly yield tetrazoles (Ber. 1907, 40, 2402):



Methyl azide $CH_3\cdot N_3$ is prepared by the action of dimethyl sulphate on sodium azide (Dimroth and W. Wislicenus, Ber. 1905, 38, 1573). Magnesium methyl iodide converts it into dimethyltriazen $CH_3N:N\cdot NHCH_3$ (Dimroth, Ber. 1906, 39, 3905).

The acyl derivatives of azoimide may be prepared by the decomposition of acyl hydrazines with nitrous acid (sodium nitrite and acetic acid):

$$C_6H_5CO\cdot NH\cdot NH_2+HONO=C_6H_5CO\cdot N_3+2H_2O$$

Tetramethylammonium azide NMe_4N_3 is prepared by the gradual addition of a solution of tetramethylammonium iodide to an aqueous suspension of a slight excess of silver azide. Tetragonal crystals ($a:c=1:0\cdot7245$). Fairly stable substance; does not explode when struck with a hammer, or ground in a mortar, or when dropped on a hot plate. Dry salt begins to decompose at about 125° (Friedlander, J. Amer. Chem. Soc. 1918, 40, 1945).

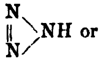
Benzoyl azoimide $C_6H_5CON_3$ (Curtius, Ber. 1890, 23, 3024 *et seq.*) crystallises in colourless tables and melts at 32° C. It explodes on heating.

This type of azide shows characteristic decompositions, two-thirds of the nitrogen being eliminated, and the residual nitrogen linking up the aromatic nucleus with a carbonyl group. Thus when gently warmed in alcoholic solution a urethane is produced, on boiling with water a di-substituted urea is obtained, and on heating the solution of the azide in benzene it is transformed into an isocyanate:

$$C_6H_5CON_3+C_2H_5OH=N_2+C_6H_5NH\cdot COOC_2H_5$$
$$2C_6H_5CON_3+2H_2O=2N_2+2C_6H_5NH\cdot COOH$$
$$=2N_2+H_2O+CO_2+CO(NHC_6H_5)_2$$
$$C_6H_5CON_3=N_2+C_6H_5NCO$$

On the decomposition of the azides of the mono and dialkyl malonic acids, and of the α-hydroxy acids, *see* Festschrift Th. Curtius, 1907, p. lxxxii.

Some controversy has arisen over the structure of azoimide, the earlier given cyclic structure having been objected to by Thiele (Ber. 1911, 44, 2522) who considers that a straight chain formation best represents the reactions of the acid:



or HN : N : N

AZOIMIDES, AROMATIC *v.* Diazo compounds.

AZOLITMIN. A substance assumed by Kane to exist in litmus (Annalen, 39, 25).

AZOMETHANE *v.* Diazo compounds.

AZOORSEILLIN *v.* Azo- colouring matters.

AZOPHENYLENE *v.* Azines.

AZOPHOR -BLACK, -BLUE, -RED, -ROSE *v.* Azo- colouring matters.

AZOPHOSPHINES *v.* Azo- colouring matters.

AZO-REDS, AZORUBINES *v.* Azo- colouring matters.

AZOTE. A name given to nitrogen by Lavoisier, and hence commonly used in French literature to designate that element.

AZOTINE. An explosive made in Austria-Hungary (J Soc. Chem. Ind. 4, 360).

AZOTOL *v.* Azo- colouring matters.

AZOTOMETER. A term applied by W. Knop to an apparatus designed to measure the nitrogen evolved by the action of sodium hypochlorite or hypobromite on ammonium salts and certain organic substances.

AZO- TURKEY RED *v.* Azo- colouring matters.

AZOVERMIN. Trade name for acetylamino azotoluene.

AZOXINE COLOURING MATTERS *v.* Oxazine colouring matters.

AZOXYBENZENE $C_{12}H_{10}N_2O$. A product of the partial reduction of nitrobenzene with alcoholic potash (Zinin, J. pr. Chem. 36, 93; Schmidt and Schultz, Annalen, 207, 325; Ber. 12, 484); or with sodium amalgam containing 3·8 p.c. of sodium (Alexejeff, J. 1864, 525; Moltschanowsky, Ber. 15, 1575).

Preparation.—Azoxybenzene is best prepared by dissolving 1 part of sodium in 25 parts of methyl alcohol, adding 3 parts of nitrobenzene and heating for 5 or 6 hours on a water-bath in a flask provided with a reversed condenser. The methyl alcohol is then distilled off and the residue treated with water, which dissolves the sodium formate formed in the reaction, and leaves the azoxybenzene as a yellow oil; this soon solidifies, and is obtained pure by one crystallisation from alcohol (Klinger, Ber. 15, 866; Moltschanowsky, *l.c.* and Ber. 16, 81; Klinger, Ber. 16, 941, footnote).

Azoxybenzene is also prepared by the reduction of nitrobenzene with arsenious oxide and caustic soda (Loesner, Eng. Pat. 1555, J. Soc. Chem. Ind. 1895, 31); by the reduction of nitrobenzene with alkali sulphides in alkali hydroxide, the products being mainly azoxybenzene and azobenzene, in proportions varying with the amount of sulphide and the time of reduction (Farb. vorm. Meister, Lucius, and Bruning, D. R. P. 216246, J. Soc. Chem. Ind. 1909, 1310); by boiling nitrobenzene with 60 p.c. aqueous sodium hydroxide and iron pyrites, or other heavy sulphides, 90 p.c. of the product being azoxybenzene (Farbenfab. vorm. Fried. Bayer & Co., D. R. P. 204653, Chem. Soc. Abst. 1909, i. 272); by heating nitrobenzene with charcoal and alkali (Farbenfab. vorm. Fried. Bayer & Co., D. R. P. 210806; Chem. Zentr. 1909, ii. 163); and by the electrolytic reduction of nitrobenzene in the presence of alkali (Farb. vorm. Meister, Lucius, and Bruning, D. R. P. 127727; Chem. Zentr. 1902, i. 446, and Farb. vorm. Weiler-ter-Meer, D. R. P. 138496: Chem. Zentr. 1903, i. 372).

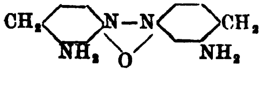
Azoxybenzene or its homologues can be obtained by heating nitrobenzene or the corresponding nitro- compound with an equal weight of zinc-dust and of an aqueous solution of calcium chloride boiling at 130°; aqueous solutions of other salts may be employed, and the reaction ensues at the boiling-point of the aqueous solution (*v.* Dechend, D. R P. 43230).

Properties.—Azoxybenzene crystallises in pale yellow rhombic needles, melts at 36°, and is soluble in alcohol or ether, insoluble in water. When heated with non-volatile substances, such as iron filings, it decomposes into aniline and azobenzene Weak reducing agents, such as sodium amalgam in alcoholic solution, convert it into hydrazobenzene (Alexejeff, J. 1867, 503): but more powerful agents, such as zinc chloride in acid solution, reduce it chiefly to aniline, a small quantity of hydrazobenzene and bases derived from it by molecular changes being also formed (Schmidt and Schultz). Azoxybenzene yields two isomeric nitroazoxybenzenes when heated with concentrated nitric acid (Linm, Annalen, 114, 217), and when heated with concentrated sulphuric acid to a moderate temperature is converted into the isomeric hydroxyazobenzene (Wallach and Kiepenheuer, Ber. 14, 2617).

In addition to azoxybenzene other azoxy-compounds have been prepared by reducing the corresponding nitro- derivatives either with sodium amalgam in methyl alcohol solution or with zinc-dust and soda (*cf.* Limpricht, Ber. 18, 1405; Klinger and Pitschke, Ber. 18, 2553; Janovsky and Reimann, Ber. 22, 41; *v.* Dechend, *l.c.*). The azoxy- compounds derived from metanitraniline, the nitrotoluidines melting at 78° and 107°, and the nitroxylidine melting at 123° yield, when diazotised and combined with phenols, amines or their sulphonic acids, a class of yellow, orange or red azo- dyes, which can be employed for cotton and wool (Poirrier and Rosenstiehl, D. R. P. 44045, 44554).

AZOXY-COLOURING MATTERS. The dyes formerly classified under this heading, of which 'sun yellow' is perhaps the best known, have been shown to be azo- dyes (*q.v.*).

***p*-AZOXY-*o*-TOLUIDINE**



is obtained by the alkaline reduction of *p*-nitro-*o*-toluidine (*q.v.*) by zinc dust or dextrose; m.p. 168°. Used in the manufacture of azo-dyes.

AZO-YELLOWS *v.* AZO-COLOURING MATTERS.

AZULENE $C_{15}H_{18}$, a hydrocarbon, an intensely blue, slightly viscid liquid, D_{25}0·9738, b.p. 295°–300° (185°–195°/25 mm.), found in the oils of cubebs, amyris, guaiacum wood, gurjun and eucalyptus, and to which their blue colour is due. When exposed to light and air is converted into a brown resin. Is soluble in sulphuric acid, giving a fluorescent solution, and forming a sulphonic acid, yielding a crystalline sodium salt, soluble in water, and giving a violet-coloured solution which becomes green when acidified. Is possibly identical with Piesse's Azulin (*q.v.*). It forms a *picrate*, m.p. 120°, lustrous black needles, by which the hydrocarbon may be identified. It appears that azulene is tricyclic and contains an aromatic nucleus, four ethylenic linkings, but no hydroaromatic conjugate double linkings, as it suffers no reduction when treated with sodium in alcohol (Sherndal, J. Amer. Chem. Soc. 1915, 37, 167 and 1537).

AZULIN. Blue colouring matter, contained in certain essential oils; *e.g.* chamomile, millefolium, and wormwood.

AZULIN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

AZURE *v.* PIGMENT.

AZURIN $C_{35}H_{32}N_4O_3$. Obtained by heating salicylic aldehyde with *o*-tolylenediamine. Colourless tables, giving blue fluorescent solutions (Ladenburg, Ber. 11, 590).

AZURITE or Chessylite. Hydrated basic copper carbonate, $2CuCO_3{\cdot}Cu(OH)_2$, forming monoclinic crystals of an azure-blue colour. Finely crystallised specimens have been found in abundance in an old copper mine at Chessy, near Lyon in the south of France, and on this account the mineral is often known as chessylite (Brooke and Miller, 1852); the name azurite (F. S. Beudant, 1824) refers to the characteristic colour. Sp gr. 3·8; hardness 3½–4. It occurs as an alteration product of copper-pyrites and other sulphide ores of copper in the upper oxidised zones of mineral veins; and it is itself often altered to malachite, the green carbonate ($CuCO_3{\cdot}Cu(OH)_2$). Fine crystals are also found at Broken Hill in New South Wales, Tsumeb in South-West Africa, and at Bisbee in Arizona; at the last-named place it occurs, together with malachite, in sufficient abundance to be mined as an ore of copper. It was also formerly mined at Burra-Burra, in South Australia. From Arizona come pretty specimens, with azurite and malachite banded together, which are polished for use in cheap jewellery. Powdered azurite was formerly used as a pigment under the name 'mountain blue,' but this is now replaced by an artificial product. L. J. S.

B

BABBIT'S METAL. An alloy of 25 parts tin, 2 parts antimony, and 0·5 part copper, used as an anti-attrition metal (*v.* ANTIMONY).

BABLAH or **NEB-NEB.** Commercial names for fruits of several species of acacia; used in the East, in combination with alumina and iron mordants, to produce various shades of drab and fawn colour in calico-printing. East Indian bablah is largely obtained from *Acacia arabica* (Willd.) (*A. indica* (Benth.)): Senegal and

Egyptian Bablah largely from *Acacia arabica* (*A. nilotica* (Delil.)). The aqueous extracts contain a red colouring matter together with considerable quantities of gallic and tannic acids.

BABUL BARK. The bark from *Acacia arabica* (Willd.) which occurs in India, Arabia, and tropical Africa: its Indian vernacular name is 'babul.' Used in India as a tanning material.

BABUL GUM. An inferior kind of gum arabic from *Acacia arabica* (Willd.). Known also as 'Bengal gum' or 'Gond babul.'

BACTERIA, CHEMICAL ACTION OF, *v.* FERMENTATION.

BADDELEYITE. Native zirconium oxide, ZrO_2, crystallising in the monoclinic system. A few isolated crystals have been found in the gem-gravels of Ceylon, and a more abundant supply of small crystals was met with at about the same time in the iron mine of Jacupiranga, in São Paulo, Brazil. The latter, at first described under the name brazilite, occur as an accessory constituent of a magnetite-pyroxene rock called jacupirangite, which is associated with the deposits of magnetite. The crystals from Ceylon are black and opaque, with submetallic lustre, but small splinters are transparent and yellowish in colour; sp.gr. 5·72–6·025; ZrO_2 98·9 p.c. The smaller crystals from Brazil range from colourless to brown; sp.gr. 5·5; they contain ZrO_2 96·52 p.c., with small amounts of silica, alumina, ferric oxide, lime, &c. The mineral has also been identified in a rock resembling jacupirangite in the iron mines of the island of Alnö, Sweden. More recently, minute crystals have been detected in a sanidine bomb rich in zircon from Monte Somma, Vesuvius, and in a corundum-syenite from Bozeman, Montana.

A massive form of zirconia occurs much more abundantly in the Serra de Caldas region of Minas Geraes, Brazil, a region characterised by the occurrence of nepheline-syenite rocks. Pebbles of compact material are here found in the diamond washings, and are known to the diamond miners as 'favas' (meaning 'bean;' other 'favas' consist of titanium dioxide). These are pale-brown, slate-grey or blackish in colour, fine-grained, and hard. Sp.gr. 4·6–5·4; they contain ZrO_2 73–93 p.c., the principal impurity being silica, with some iron, alumina, and titanium. In the same region there has also been found, as a crust on weathered augite-syenite, mamillated or reniform masses with a radially-fibrous structure and concentric banding. It contains ZrO_2 97 p.c., and has sp.gr. 5·538. This variety appears to occur in considerable quantity, and in lumps weighing several kilograms. E. Hussak, in 1899, referred the massive form occurring as 'favas' to baddeleyite, but he was inclined in 1903 to regard the fibrous variety as a distinct modification of zirconia. The latter has recently been sold in America under the trade name *zirkite*, and it is stated to consist of a mechanical mixture of baddeleyite, zircon, and a new zirconium silicate. The mineral possesses a high degree of infusibility, high resistance to basic and acid slags, low thermal conductivity, and a very low coefficient of expansion. It is thus eminently suitable as a refractory material for the construction of crucibles, muffles, fire-bricks, and furnace linings. It is also employed as an opacifier and as an abrasive. (W. T. Schaller, Mineral Resources, U.S. Geol. Survey for 1916, 1917, ii. 377; A. Granger, Chem. News, 1919, 118, 115.)

L. J. S.

BADISCHE ACID. 2-naphthylamine-8-sulphonic acid. *V.* NAPHTHALENE.

BAEL FRUIT. The dried half-ripe fruit of *Ægle Marmelos* (Correa), from Malabar and Coromandel; is used in diarrhœa and dysentery, and the fresh pulp is sometimes employed as a laxative.

BAEUMLERITE. A potash-salt mineral found as thin bands in the rock-salt of the Desdemona salt mine in the Leine Valley, Prussia (O. Renner, 1912). It is colourless and transparent, extremely deliquescent, and has the composition $KCl{\cdot}CaCl_2$. F. Zambonini (1912) has suggested that this is identical with the Vesuvian mineral 'chlorocalcite,' first described by A. Scacchi in 1872, and later proved to be cubic and with the composition $KCl{\cdot}CaCl_2$.

L. J. S.

BAGASSE, BEGASS, or MEGASS. Terms applied to the refuse sugar-cane after crushing.

BAKELITE. A condensation product of phenol, cresol or other phenolic bodies, and formaldehyde, paraformaldehyde, hexamethylenetetramine, or other substances with a reactive methylene group, mixed with asbestos or some form of cellulose, and heated so as to convert it into a solid infusible resinoid mass capable of being moulded or worked.

In the actual manufacture of bakelite ordinary commercial carbolic acid, which consists largely of cresols, is employed, in connection with small quantities of various alkaline substances, which appear to act catalytically in promoting the action of the formaldehyde. The first products obtained are semi-solid resin-like bodies which under the influence of heat and pressure become hard, insoluble and infusible, and of a high chemical and mechanical resistance. This initial stage is variously termed 'Bakelite A, Liquid or Solid,' Resinil mass, &c. The final product is known as 'Bakelite C,' 'Resinite,' 'Condensite,' or 'Resite.' It is regarded by Baekeland, with whose name the invention and commercial application of the substance is associated, as a polymerised hydroxybenzylmethyleneglycolanhydride. To form it 'Bakelite A' is heated in a modified form of autoclave to about 170°, under pressure produced by compressed air or an inert gas, such as carbon dioxide. Instead of the autoclave the Bakelite A, after being mixed with the appropriate fibrous material, may be placed in a steel mould, and gradually hardened in a hot press during from 1 to 2 hours, at a temperature between 100° and 200°.

Bakelite C in its purest form is a colourless or light golden-yellow mass of sp.gr. 1·25. It is a bad conductor of heat and electricity, and a first rate insulating material. It resists pressure and shock, but has a comparatively low elasticity. It can be heated to 300° without change. At a higher temperature it chars, but does not inflame. It is non-hygroscopic, and resists the action of concentrated hydrochloric acid, oil of vitriol, nitric acid and bromine. It is less resistant to the action of alkalis. From the ease with which it can be worked it can be used for a great variety of articles, such as switch-boards, telephone receivers, armatures, and commutators for dynamos and motors, phonograph records, mouldings for kodaks, photographic developing trays, &c. Also for the manufacture of billiard-balls, razor handles, umbrella and stick handles, pen and pencil holders, cigar and cigarette holders, pipe mouthpieces, ornaments and beads for jewellery, &c. (Lebach, Jour. Soc. Chem. Ind. 1913, 32, 559).

The conditions of the formation of bakelite have been investigated by Matsumoto (J. Chem. Ind. (Tokyo) 18, No. 207), who found that all stages of the reactions are greatly accelerated by small additions of various substances. The best results, as regards yield and quality of product, were obtained by the use of sodium hydroxide and ammonia as condensing and hardening agent respectively. Sulphuric acid, hydrochloric acid, ammonia, hexamethylenetetramine, aniline, sodium sulphite and sodium carbonate were also satisfactory as condensing agents, but only basic substances, such as alkali hydroxides or ammonia were suitable as hardening agents (Jour. Chem. Soc. Ind. 1915, 34, 1104).

The General Bakelite Co. has a very complete plant at Perth, Amboy, and there are a large number of licensees in the United States; bakelite plants in Germany, France and England, and several factories where bakelite goods, such as buttons, are manufactured under licence.

Bakelite is amber-yellow when freshly made, but gradually acquires a wine-red colour under the action of daylight. If the red colour is not too strong it may be discharged by heating to 100°–150° for several hours. This colour change has proved objectionable when the substance is used for ornamental purposes (imitation amber), and has led to its abandonment in certain trades (Newbery and Lupton, Manchester Memoirs, 62 (1918), 13).

BAKERITE. A hydrated borosilicate of calcium, $8CaO{\cdot}5B_2O_3{\cdot}6SiO_2{\cdot}6H_2O$, containing B_2O_3 27·7 p.c. It is massive and snow-white, sometimes with a greenish tinge, and resembles unglazed procelain or fine-grained marble in appearance. D 2·73–2·93, H 4½. It occurs with howlite as veins and nodules of considerable size in the borate mines in the Mohave Desert, sixteen miles north-east of Daggett, in San Bernardino Co., California (W. B. Giles, Mineralog. Mag. 1903, xiii, 353). L. J. S.

BAKHAR. an artificial ferment prepared from rice, powdered roots and other parts of certain plants, by Indian natives, and used in the production of Hindu rice-beer (pachwai), and of the spirit distilled from it. It contains many varieties of moulds and fungi capable of saccharifying starch, of which the most active is *Aspergillus oryzæ*, and several yeasts capable of producing alcohol (Hutchinson and Ram Ayyar (Jour. Soc. Chem. Ind. 1916, 35, 751).

BAKING POWDERS are any powders used as substitutes for yeast. The bread or cake is rendered spongy by the carbon dioxide generated in the dough; this is effected by the action of an acid, such as tartaric acid, on sodium bicarbonate, and some farinaceous substance is added to act as diluent. To permit the use of discoloured flour, alum was frequently employed, this renders the bread white, but at the same time indigestible. In 1899 such articles as baking powder were included in the Sale of Food and Drugs Acts, and therefore the use of alum or any injurious matter was prohibited. All articles are perfectly dried before mixing, passed through a fine sieve, and kept in air-tight packages in a dry place. To every pound of flour, 1 teaspoonful of baking powder is added for bread, and 2 teaspoonfuls for cakes. General preparations are:

(1) 6 ozs. tartaric acid, 2 ozs. sodium bicarbonate, and 1·5 ozs. of farina.

(2) 16 ozs. sodium bicarbonate, 14 ozs. tartaric acid, and 6 ozs. magnesium carbonate, and 12 ozs. farina (Workshop Receipts, 1909).

(3) 2½ lbs. cream of tartar, 2½ lbs. sodium bicarbonate, 1 lb. acid calcium phosphate, and 4 lbs. cornflour (Pharm. Formulæ, 1908, p. 322).

(4) 3 lbs. acid potassium sulphate, 1 lb. sodium bicarbonate, and 1 lb. of cornflour (Pharm. Formulæ, 1908, p. 322).

(5) 5 ozs. tartaric acid, 15 ozs. cream of tartar, 20 ozs. sodium carbonate, and 40 ozs. rice flour (Workshop Receipts, 1909, p. 90).

(6) 20 parts acid sodium phosphate, 20 parts acid calcium phosphate, 25 parts sodium bicarbonate, and 35 parts starch (Hiscox, 1907, 102).

Crampton's powder: 2 parts cream of tartar, 1 part sodium bicarbonate, and 1 part corn starch.

Rumford's powder: (approx.) 7 ozs. sodium bicarbonate, 14½ ozs. sodium phosphate, and 3½ ozs. starch.

Royal powder: A mixture of cream of tartar, tartaric acid, sodium bicarbonate, and starch.

Goodall's powder is a mixture of 2 parts rice flour with 1 part tartaric acid and 1 part bicarbonate of soda.

Green's powder: 35 lbs. tartaric acid, 56 lbs. of sodium carbonate, and 1 cwt. of potato flour.

Horsford's powder consists of 2 packets: (1) acid calcium and magnesium phosphates, made up with a certain quantity of flour; (2) bicarbonate of soda with a little potassium chloride.

Borwick's powder is an artificial fermentation powder compounded with coarse maize.

Self-raising flour may be prepared by mixing 8 ozs. sodium bicarbonate, and 18 ozs. cream of tartar with 1 cwt. of flour.

Milk in the solid form, concentrated in a vacuum at 50°–60°, was used by Hooker, to replace inert farinaceous matter. It is claimed to have a better nutriment value and increased leavening power: 20 parts tartaric acid, 54 parts milk powder, and 1 part moisture. The soda is added before the milk is completely dry, then the whole dried and ground finely in a mortar (J. Soc. Chem. Ind. 27, 1908). Cream of tartar is soluble in hot water, but only slightly so in cold, whilst tartaric acid dissolves readily. Therefore a powder containing cream of tartar evolves carbon dioxide much more slowly than one compounded with tartaric acid. This is advantageous, as a dough containing it can be kept for some time before baking, also it does not darken the bread; on the other hand, it forms Rochelle salt which has a very slight saline taste. The best powders are made from a mixture of tartaric acid and cream of tartar. Good substitutes for tartaric acid are acid ammonium phosphate, and acid potassium sulphate, acid potassium and calcium phosphates, but they have a tendency to darken the bread. The acid calcium phosphate used in baking and self-raising flours occasionally contains an undue amount of calcium sulphate (J. M. Hamill, Report of the Local Gov. Board, 1911, Food Report, No. 13).

Ammonium carbonate is used in very light pastries, but it requires expert handling, and so is very rarely present in the make-up preparations.

BAKUIN. Russian mineral machine oils; recommended for lubricating heavy machinery on account of their high viscosity and great power of resisting cold (Seifenseid, Zeit. 31, 366; 32, 378; J. Soc. Chem. Ind. 3, 181).

BAKUOL. A name given by Mendeléeff to an illuminating oil, prepared from the crude oils of Baku by mixing ordinary kerosene of sp.gr. 0·82 to 0·83 and flashing point 20° to 30°, with the so-called intermediate oil, which has a sp.gr. of 0·86 to 0·88 at 15°, and is not inflammable at 100°. The mixture has a sp.gr. of 0·84 to 0·86, and flashes at temperatures varying from 50° to 70°. From 100 parts crude naphtha 20 to 30 parts of kerosene and 10 to 20 parts of intermediate oil can be obtained.

The following table gives the sp.gr., flashing-point, and luminiferous value of four bakuols examined by Ilimow:—

Specimen of oil	Sp. gr. at 17·°5	Flashing point at 760 mm.	Candle-power	Consumption per hour in Russian lbs.	
				For the lamp	Per candle power
No.					
1	0·8280	36·0	7·40	0·0588	0·0080
2	0·8310	37·5	10·40	0·0633	0 0060
3	0·8360	39·5	9·84	0·0633	0·0064
4	0·8310	49·5	8·30	0·0675	0·0081

Literature.—Mendeléeff, Zeitschr. Technik, 1886, No. 109; Chem. Zeit. 1883, 231; Ilimow, *ibid.* 10, 1459; J. Soc. Chem. Ind. 2, 238; 5, 661; 6, 135 (*v.* PETROLEUM, RUSSIAN).

BAKURIN. A lubricating oil, prepared by mixing 100 parts of crude Baku oil with 25 parts of castor oil and 60 to 70 parts of sulphuric acid of 66°B. After standing the mixture is stirred two or three times with water, the water run off, and the oil treated with soda or potash (Müller, D. R. P. 35141, Dingl. poly. J. 200, 240).

BALANCE. A generic term, designating a variety of machines for ascertaining the weight of a body in terms of the weight, at the time and place, of a standard *mass* (gram, ounce, pound, &c.), and thus determining its mass. By means of a balance and a set of 'weights,' we ascertain that a body has P times the weight of the unit piece of the set, and conclude that its mass is P times the mass of this piece likewise, whatever the chemical nature of the body may be. In justification of this inference we might refer to Newton's pendulum experiments, or to the often proved chemical axiom that the weight of any body or set of bodies is independent of the state of combination of its elements. But from the standpoint of the chemist it is sufficient to know that, supposing even each element had its own factor for converting 'weight' into mass, it would still follow that the weight of a body, however complex, is equal to the sum of the weights of what in any sense we may call its 'components,' and that the ratio of the weight W_1 of a body of fixed elementary composition to the weight W_2 of another body of even a different fixed composition is as constant, although perhaps not equal to the ratio of the masses $M_1 : M_2$. Of all balances the equal-armed lever balance, often called '*the* balance' *par excellence*, is by far the most important.

The balance exists in a variety of forms, all of which seek to realise the same ideal machine. An absolutely rigid beam, so suspended that whilst it can rotate freely about a certain axis (which goes across it somewhere above its centre of gravity, and of which every point holds a fixed position in reference to the stand) it is not capable of any other motion. From two points, *a* and *b*, which lie in the same plane as the axis of rotation—one near the left, the other near the right end of the beam—the pans are suspended by means of absolutely flexible linear strings. *a* and *b* are equidistant from the axis of rotation. So far all balances are alike. In now passing to the actual instrument, we shall confine ourselves in the main to the class of balances known as precision balances.

Of the difficulties involved in the construction of such balances, that of producing a sufficiently light and yet practically inflexible beam, seems to have rested most heavily on the minds of the earlier makers; but there can be no doubt that many of their efforts in this direction, which occasionally resulted in what we should now call fantastical beam-forms (hollow ellipsoids, monstrous skeleton-forms, &c.), must be traced back to their inability to reach a sufficient degree of precision in the geometric adjustment of the three pivots, and to their charging against the flexibility of the beam what was really owing to these defects in the adjustment. As these difficulties were overcome, beams assumed less fantastic forms. Sacré of Brussels, we believe, never uses any but plain rod-shaped beams (only perforated in the middle to insert the bearing of the central knife). Most balance makers, however, prefer the form of a largely perforated rhombus or isosceles triangle (cut out, virtually, of a plate of metal), and thus attain all that is needful without offending the eye by unduly stretching the middle section, and without using anything more intrinsically rigid than hammered brass or some kind of bronze. In reference to ordinary chemical balances (for charges up to say 100 grams), it would be no great exaggeration to say that any reasonably made beam is sufficiently rigid; only in the case of balances intended for very high charges, such as 5–10 kilogrammes, is it at all worth while to employ refinedly designed beam-forms, or to look out for a material of exceptionally high rigidity. For these particular balances hard steel would be the best material; but, unfortunately, steel beams are apt to become magnetic. With small assay-balances intended for charges up to, say, 5 grams, on the other hand, the question of rigidity is practically out of court, and the use of an exceptionally light material—such as aluminium, or, better, that alloy of 95 parts of aluminium and 5 of silver (which Sartorius of

Göttingen uses for small balances generally) is indicated.[1] In all balances the axis of rotation is realised in a straight knife-edge ground to a prism of hard material, which is firmly fixed to the beam, traversing it crosswise and resting on a hard bearing. In ordinary balances the middle knife is simply driven through the beam, and only its two ends are supported in cylindrical, or, what is better, roof-shaped bearings, which form secures to the edge a sufficient fixity of position, forward and back sliding being prevented by cutting off the ends of the knife obliquely, so that the edge terminates in two points, and closing the bearing at each end by a steel plate, so that the knife has just room between without jamming. In suspended balances the central bearing is fixed at the lower end of a light framework, terminating above in a hinged-on ring for suspending the instrument from a fixed hook or the thumb of the operator.

In all precision balances the central bearing is attached to a fixed pillar, and is plane; in the best balances the bearing is made of one piece, and the central knife-edge rests upon it in its entire length. A plane bearing necessarily involves an arrestment so constructed that, besides doing its primary duty, it assigns to each point of the central knife-edge a fixed position on its bearing. In former times hard steel was used exclusively for both knives and bearings; subsequently agate bearings came to be combined with steel knives. Robinson of London was the first to make both knives and bearings of agate. The agate knife adds nothing to the precision of a newly-made balance, but it always remains clean, while a steel knife, in a chemical laboratory more especially, is apt to rust. Steel knife-edges are generally ground to an angle of 60° (or 90° for very heavy charges). In agate knives, as made by Oertling, only the body of the agate prism is ground to 60°, while the edge is formed by two narrow facets, inclined to each other at a far more obtuse angle. Such an obtuse edge stands many years' constant use without wearing out. American makers have introduced the artificially made osmium-iridium, which is used for the tipping of stylograph pens, as a material for both knives and bearings.

For the realisation of the two point-pivots A and B, a great many combinations have been invented. A now obsolete construction of Weber's (Bib. 2) adapts itself very closely to our ideal conception. He provides the beam at its two ends with knife-edges turned sideways and suspends the pans by means of threads of unspun silk which are fixed somewhere in the back of the beam and hang over the edge. The axis of rotation is realised similarly. In ordinary balances, as a rule, a vertical slit is cut into each end of the beam, and this is traversed by a short prismatic knife, the edge of which is a circular arc of small radius which stands perpendicular to the line AB. From each such knife the pan is suspended by means of an 8 or 2-shaped steel hook. This construction, if well executed, may afford high precision, but the suspender-hook is apt to rub against the sides of the slit in the beam. Hence, wherever the hook-and-eye arrangement is adopted for precision balances, it is modified in this sense, that the knife-edge forms a circle of relatively large radius which lies entirely outside the body of the beam. This system, compared with those considered in the sequel, offers the advantage of easy adjustment. It used to be very popular with balance makers, and many excellent instruments have been produced with it especially by Deleuil of Paris. For small assay-balances it is indeed probably as good as any other that could be named; for balances intended for higher charges it does not possess sufficient durability, although, as the writer is able to say from his own experience, if well made, it lasts better than is generally supposed. In modern balances it is rarely seen; in these, as a rule, the pans are suspended from long straight knife-edges, similar to the central one, by means of broad bearings which, of course, must be arranged so that they neither twist nor slide. A very efficient and easily made arrangement is to give the bearing the form of a roof cut and of one side of a prismatic block of steel or agate, and to fix it to the upper end of a stirrup-shaped or ⅂-shaped holder which terminates below in an eye, from which the pan is suspended by a suitable hook. The eye stands at right angles to the knife-edge; its working point, when the instrument is in use, lies vertically below the centre of the respective end-edge, and the effect is the same as if the whole of the load were concentrated in that one centre-point, although the pressure of the bearing on the knife is equally distributed over the whole of its working length. This hook-and-eye arrangement is absolutely indispensable if the pans are suspended by stiff stirrups, because, if these were rigidly connected with their bearings, the virtual point of application of the load would shift forwards and backwards on the edge, and the least want of parallelism between it and the axis of rotation would cause the balance to give inconstant readings.

These roof-shaped bearings were formerly used almost exclusively by German makers, although an undoubtedly superior system had been introduced successfully by Robinson of London many years ago. In it the pans are suspended by *plane* bearings which a suitable extension of the arrestment keeps in their right positions. Robinson's balances were justly famous in Great Britain—a few of them are still working to this day—yet, after Robinson's death, Oertling was almost the only balance maker who followed him in this respect. The general plea against the system was that flat end-bearings were liable to twist; and some, after having adopted Robinson's plan, 'improved' upon it by cutting out a central portion of each end-knife, so that it worked only with its two ends; proving thereby that they did not understand their business, because a *really plane* bearing, as a matter of fact, does *not* twist on a *really straight* knife-edge, even if the pan oscillates strongly. The principal advantage of the Robinson system is that it enables one to do what the roof-shaped bearing prohibits, namely, to satisfy himself that the knives and bearings are geometrically perfect. But here, as in all analogous cases, we must not forget that the excellence of an instrument—supposing it to be based on a reasonable system—depends far more on the skill of the maker than on the theoretical perfection of the design.

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[1] For a fuller discussion of this subject, *v.* the writer's Memoir (Bib. 6, 322).

From the bare realisation of the ideal machine, we now pass to the accessories which a balance needs in order to become a convenient instrument, and we will consider these in the order of their importance.

The arrestment is a mechanical contrivance to enable the beam to be arrested at any point of its angular motion, and to bring it to permanent rest in its '*normal*' position, in which the plane of three axes stands horizontal. If the three pivots are self-adjusting, there is, strictly speaking, no need of an arrestment; still for the rapid execution of precise weighings it is almost indispensable.

If the central bearing forms part of a suspended frame, an arrestment is easily devised in the ways illustrated by Figs 1 and 2. Fig. 1 explains itself; in Fig. 2 the balance is hinged on to the bent-down end of a flat bar which slides up and down in guides fixed to the pillar between two beds of rollers 2×2 in the guides on the front side of the bar, and one which is pressed against its back by a spring. At its lower end the bar has a small wheel which rests on the shorter end of the hinged lever by means of which the balance is raised or lowered. A small vertical adjusting screw below the shorter end of the lever defines the lowest position of the bar at which the pans just touch the table without slackening the chains. In either case it is an improvement to suspend a heavy block of metal at the lower end of the frame, to compel it to hang plumb, and to hinder it from oscillating. The specific advantage of *suspended* balances is that they need no horizontal table or levelling screws at the board on which they may be erected. But pillar-balances are on the whole more convenient. In the case of these (supposing plane bearings to be absent) a good system is to fix the central bearing to the top of a rod which slides up and down within the pillar—properly guided to prevent shaking and rotatory motion—and, with its lower end, rests on an eccentric concealed in the sole and governed by a lever- or disc shaped handle. The eccentric must be so adjusted that when it is at one of its extreme positions, the pans just touch the board and no more, while, when it is in its other extreme position, the beam is at its maximum angle of free play. In the excellent *Tarirwaagen* of Messrs. Becker's Sons, Rotterdam, this system of arrestment is realised to perfection.

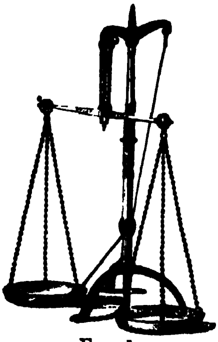


FIG. 1.

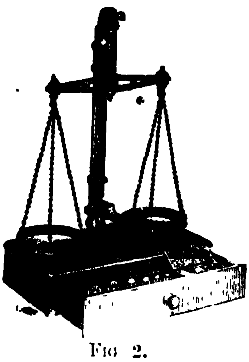


FIG. 2.

The system needs only be slightly modified to adapt itself to the case of a plane central bearing, but we prefer to at once pass to the case of *three* plane bearings, and in doing so cannot do better than describe a balance (for charges up to 5 kilos.) which Mr. Oertling made for us some years ago. As shown by Fig. 3, the instrument rests on three pillars standing on a hollow square block of iron which conceals the eccentric. Firmly fixed to the top ends of the pillars is a substantial brass frame which terminates at its two ends in V-shaped supports for the end-bearings. These latter are agate plates cemented each to the horizontal bar of a kind of stirrup, the bar terminating on each side in a cylindrical steel pin which, when the balance is at rest, lies in the corresponding V of the frame. The central pillar conceals a movable steel rod, provided at its lower end with a wheel which rests on the eccentric. Its upper end carries a substantial brass block which divides into two short piers above, whilst it expands below into a horizontal plate, pierced by a circular perforation near each end. These perforations fit exactly around two cylindrical steel pins, *r*, *r*, fixed to the top plate of the pillars, so that the rod, when moving up or down, cannot turn or shake in the slightest degree. The space between the two piers is bridged over by the central bearing, a plane agate plate fixed to a prismatic piece of brass, which is dovetailed into the tops of the piers, so that, while perfectly steady when in its place, it can without much effort be slid out or in (Fig. 4). It is inserted while the beam is being held in its intended position and passes through a large perforation in the beam into which the middle knife projects. The beam terminates at its left end in one, at its right end in two, horizontal steel pins whose shoulders are continuous but rapidly expanding surfaces of rotation, and these pins fit, the single one into a notch, the couple into a fork, forming part of the fixed arrestment frame. In the arrested balance each bearing is almost in contact with its knife; if the eccentric be now turned, the central bearing rises and lifts the whole, beams and end-bearings, to a greater or less height, and ultimately into that maximum height at which the eccentric stands still without being *held* in its position. If the eccentric be now turned the other way.

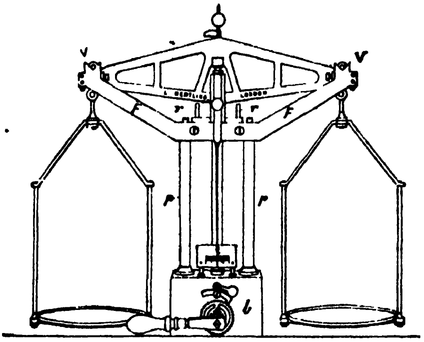


FIG. 3.

both the beam and the end-bearings fall back, ultimately, into their prescribed positions of rest, even if they should have twisted, which, however, they never do in the instrument under description. For a balance intended for quick work, and more especially for one used occasionally for the weighing out of predetermined quantities of solids or liquids, this system of arrestment is the best that we know of, because it enables the instrument to be handled pretty much like an ordinary pair of scales; only, to be able to do so to the best advantage, and without spoiling the terminal pivots, the pans must be suspended by flexible short-linked chains whose length is so adjusted that the pans just touch the table when the balance is fully arrested. Stirrup-shaped pan-suspenders (as represented in the figure) are more convenient than chains in many respects, but, for the purpose under consideration, they do not work with plane end-bearings. The ratchet-wheel visible in the figure was intended to enable the eccentric to be arrested at intermediate positions (in taring with garnets and similar operations) but was found not to work satisfactorily; it is simpler and better to have a block of wood so adjusted that when put under the handle it just raises the beam sufficiently to enable one to see which side goes down.

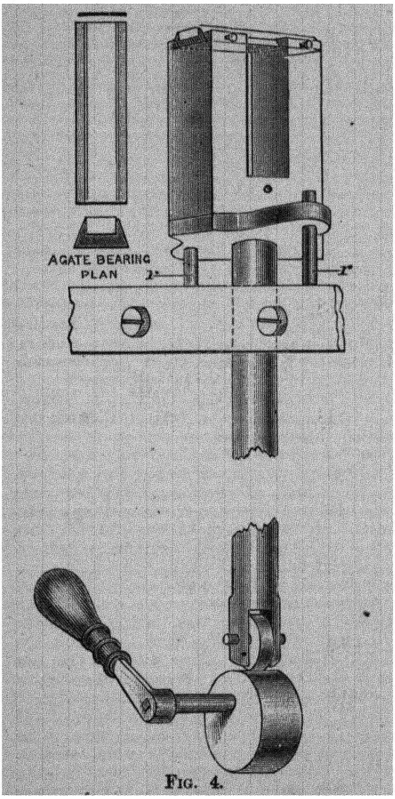
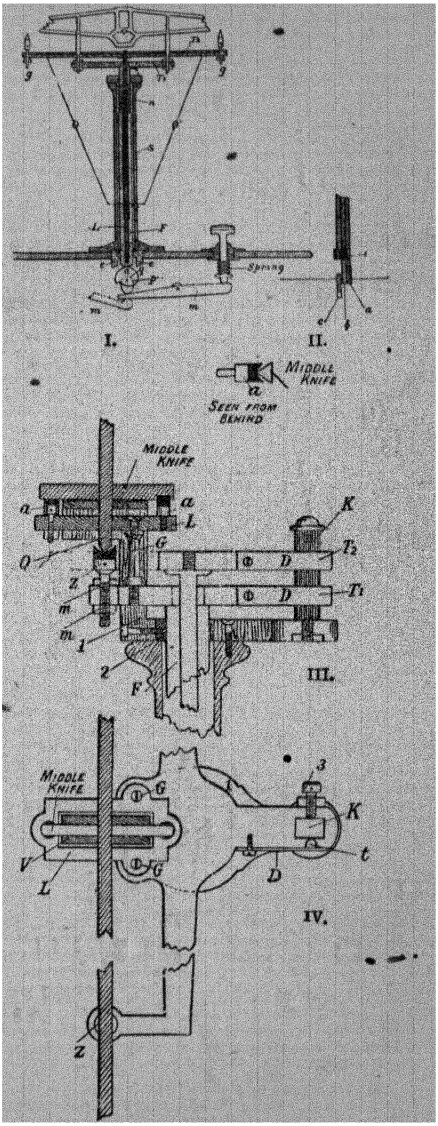


Fig. 4.

Instead of fixing the arrestment frame to the pillar and making the central bearing movable, we may of [illegible] the reverse, and this latter system, indeed, is generally preferred for precision balances of a higher order.



III. Section through pillar and middle knife; IV. Horizontal projection.

Fig. 5.

The kindness of Messrs. C. Staudinger's Nachfolger of Giessen, Germany, enables us to give a detailed description and drawing of the kind of movable frame arrestment which they are in the habit of applying to their best instruments.

As shown by Fig. 5 (I. to IV.) the pillar is hollow and accommodates a round bronze rod F. This rod itself, however, conceals a co-axial round rod L of nickelled steel. The bronze rod F, at its lower end, is guided by perforated blocks, *e*, *e*, Fig. I., while at its upper end it terminates in a thinner cylinder surrounded by a gently acting spiral spring *n*. The head of the pillar is perforated and guides the attenuated end of F in its up-and-down motion. The inner (steel) rod, L, is guided similarly within the bronze rod F and has a spring *i*, Fig. II., about its lower end to assist its natural tendency to sink. The two rods F and L carry two independent arrestment-bars; L the bar T_2 for the end-bearings, F the bar T_1 for the beam.

A square pillar K (Figs. III. and IV.), which rises from a prolongation of the head of the stand pillar S, by passing through perforations in the two bars T_1 and T_2, prevents any motion of these about the axis of their rods. As shown by Fig. IV., an adjusting screw, passing through the bar, and a flat spring *t* on one side of the square perforation of the bar (T_1 or T_2), enforce steadiness of motion.

The upright pins *g g* (I.), which are tipped with sharp agate cones, arrest the end-bearings by rising into corresponding conical hollows in the latter. (Fig. 6, though taken from an Oertling balance, will give an idea of the way in which these pins work.) The two slanting lines O O (Fig. I.) are meant to indicate two supports, which pass through slots in the pillar S and the bronze rod F, and are fixed to the inner rod L, to lend additional rigidity and steadiness of motion to the end-bearings arrestment.

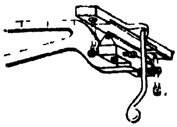


FIG. 6.

The arrestment of the beam is effected by two adjustable piers Z rising from the bar T_1 of the bronze rod. The tops of these piers carry roof-shaped agate bearings, in which the arrested beam lies with its lower (bevelled) edge. This would be sufficient to keep the beam from turning. To hinder it from moving progressively, there is a horizontal frame L (Figs. III. and IV.) united with bar T_1 by two little pillars G, G, and carrying two agate bearings, a roof-shaped one at the hinder end and a plane one at the front end of the middle (agate) knife. The roof-shaped bearing receives that end of the middle knife as the roof-shaped bearing of an ordinary balance would (so that by it, and the two beam-supports, three points of the arrested beam are fixed in prescribed positions); the plane bearing in front only supports the knife as it rises up to it on arresting. This plane bearing is adjustable by means of a screw, so that the arrested central knife-edge can be made rigorously parallel to the fixed central bearing of the working instrument.

There are three eccentrics, all attached to the same axis and governed by the same handle (Fig. II.), one, A, for the bronze rod F, a second, B, for the inner steel rod L, and a third, C, for a pan-arrestment, whose mode of acting will readily be seen by a glance at Fig. I. When the handle stands so that line *p* (Fig. I.) is vertical the beam is arrested; after this point has been passed, the beam-supports remain at the same altitude, but, on turning the handle further, bar T_2 is raised to lift the terminal bearings as soon as line *q* stands vertical. The last third of the motion of the handle arrests the pans.

The principal feature in Messrs. Staudinger's Nachfolger's arrestment obviously is the relative independence of the beam-arrestment and of the end-bearings arrestment. In most other movable frame systems there is only one frame for both, and things are arranged so that the middle edge is held fast after the end-bearings have been lifted by a hair's breadth, and that the upward motion comes to an end as soon as the middle knife is just visible above its bearing. A refinement upon this construction is to merely effect the three contacts, and then, by means of a special eccentric, to let the middle bearing drop through a distance of 0·1 or 0·2 mm.

Whilst all the several points of a rigid though movable arrestment-bar move up and down in vertical straight lines, the end-edges of the vibrating beam describe circular arcs. Hence whenever the bar is raised against the *slanting* beam, the end-bearings *tend* to slide over their knives and to spoil them. To preclude the possibility of this, Becker & Sons, in their finest balances, make the bar for the end bearings arrestment of two halves which are hinged on to the pillar in or very near the axis of rotation. Sartorius adopted this system and brought it into a slightly different form, regarding which we refer to Bibl. 4, where it is illustrated by a drawing.

In a balance which has only plane bearings, no kind of arrestment, of course, will give satisfaction, unless its several parts, and also the pillar and the sole, are sufficiently substantial to ensure absolute constancy of configuration and absolute steadiness of motion even after long-continued use. The old masters used to pay great attention to this important point, but it is sadly neglected by the majority of their present successors.

In a balance of which the end-pivots are self-adjusting, the movable arrestment frame assumes a very simple form. All that is needed is a small frame bearing V-shaped notches for arresting the middle knife in a prescribed position, and fixed to a horizontal bar with two projecting pins, in order, at the same time, to support the beam in a horizontal position. As these pins have no other function, the bar may be very light, and the whole system need not have that absolute steadiness of motion which is indispensable in the case of plane end-bearings.

The needle and scale serve to define the angular position of the beam. In all modern precision balances the needle points downwards, and is meant to embody a straight line passing through the axis of rotation and standing perpendicular on the line connecting the two point pivots A and B. The scale is attached to the pillar; its zero, if the stand is properly levelled, lies vertically below the axis of rotation. To enable the stand to be levelled, there must be either a plumb line or two spirit levels *fixed to the pillar*, and so adjusted that when they point to their zeros, the line connecting the zero of the scale with its projection on the middle edge is vertical. The scale should be so graduated that the needle-line, if produced, would cut, not the circle described by the needle's reference point, but the horizontal tangent to this circle, into pieces of equal length (*v. infra*). In most practical cases, however, this comes to the same as saying 'into pieces of equal angular value.' In balances provided with a fixed arrestment frame the scale should be made to move up and down with the beam, so that its position in reference to the needle remains constant. In most balances the end-point of the needle is just clear of the upper circular edge of the scale, but it is better to make its lowest portion almost linear, and let this project over the scale and almost touch it.

The rider.—Small weights are difficult to handle and easily lost. To avoid this inconvenience, Berzelius conceived the happy idea of dividing the right side of the beam, or rather the horizontal lever arm corresponding to it, into ten equal parts, and substituting one rider weighing ten centigrams for all the centigram and milligram pieces of the set of weights. Obviously the rider, when suspended at the first, second, &c. mark from the centre, acts like 1, 2, &c. centigrams placed in the pan, and it is equally obvious that every tenth of a division on the beam corresponds to one milligram of additional weight. This system was universally adopted and is still in use, only with this qualification, that we now apply it to the counting of the milligrams by means of a rider weighing ten milligrams. The reason for the change is obvious. In most balances the points 0 and 10 of the rider-scale are inaccessible. Becker & Sons avoid this inconvenience by dividing the arm into twelve parts, and supplying a rider weighing twelve milligrams. Other makers, for instance, Messrs. Verbeek & Peckholdt, of Dresden, make the top bar of their beams exactly horizontal, and, besides keeping it clear of impediments, make it project beyond the terminal edges. One of the advantages of this system is that, in the case of a short beam, it enables us to double the degrees of the rider scale, by dividing each arm into only five (integer) parts, numbering these from the left knife onwards and using a rider weighing five milligrams. Only, if we do so, the rider suspended at the zero must be counted part and parcel of the instrument. Bunge provides a special rider-bar so contrived that the path of the rider lies in the plane of the three axes. This, *theoretically*, is the most perfect arrangement.

A rider arrangement, to be complete, must be supplemented by a mechanical contrivance enabling one to shift the rider while the balance case is closed, and to do so with greater rapidity, ease, and certainty than would be afforded by a forceps, supposing the case to be open. Rider-guides fulfilling this latter condition are scarce; even with the best the rider drops down occasionally, and has to be searched for.

To avoid this source of annoyance Hempel does away with the rider and substitutes for it a vane with a limb graduated into milligrams (*v. infra*).

The gravity bob—a small button or disc of metal so attached to a wire standing vertically on the top of the beam exactly above the axis of rotation that it can be screwed up and down along the whole range of the wire. It enables one to raise or lower the centre of gravity of the beam, and thus to establish any desirable degree of sensibility.

A bob thus constructed meets all the requirements of the balance maker, but for the chemist who uses the balance it is desirable to have an arrangement which enables him at a moment's notice to establish any predetermined degree of sensibility. Such an arrangement was invented by the writer some years ago (Bibl. 8 and 5). It consists of a small bob fixed by mere friction to the upper end of the needle, which at that part has the form of a triangular prism, and is provided with a graduation. The mode of standardising the scale is explained below.

Some arrangement for establishing perfect equilibrium in the unloaded instrument is required. A small bob screwing along a horizontal wire fixed to some convenient part of the beam answers best. Less convenient is a 'vane,' meaning a little movable horizontal lever attached to the lowest point of the wire, which carries the ordinary gravity-bob, or to the upper part of the needle. To understand the working of the vane—and at the same time that of Hempel's invention above referred to—substitute for the vane an equivalent rigid line (Fig. 7). If the vane-line stands in the position OO—*i.e.*, if it is parallel to the middle knife—it adds no weight to either side, if turned through 90° into position O (10), it virtually adds, let us say, 10 milligrams to the charge of the right pan. Divide the line O (10) into ten equal parts, erect an ordinate in each point, and you find the points 0, 1, 2, 3, &c., of the circular path of the end-point of the vane, to which the vane-line must point, if the virtual addition to the right pan is to be equal to 0; 1, 2.... 10 milligrams. A glance at the figure shows one weak point in the vane contrivance. There is, however, no need of our dividing the circular limb exactly in the way of our figure. We may, for instance, place the zero at the −7 and the ten at the +7 of our figure, divide the interval between the projections on line (10) ($\overline{10}$) of +7 and −7 into ten equal parts, and so adjust the mass of the vane and its distribution that, by turning it from the new zero (at −7) to the new '10' (at +7), we virtually add 10 milligrams to the right charge. The degrees, corresponding each to 1 milligram, then become so nearly equal to one another that

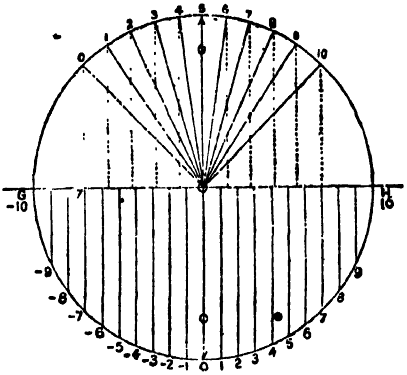


Fig. 7.

the subdivision of each into ten parts of equal angular value is permissible.

THE THEORY OF THE BALANCE.

For a first approximation imagine a balance which is ideally perfect, and assume it to be charged with P grams from the left and with P grams from the right point pivot. The balance, when free to vibrate, can remain at rest in only its normal position, and if brought out of it will vibrate about it as a pendulum, because the two charges are equivalent statically to one heavy particle weighing. 2P, situated in the central knife-edge. Now, put a small overweight Δ on, say, the right pan; the position of potential rest will shift, and the beam, to reach it, must turn (downwards on the right side) through a certain angle α, which depends only on Δ and on the weight W of the empty beam, which latter we may assume to be concentrated in its centre of gravity c, the force 2P being obviously out of consideration. But the two weights, Δ at *b* and W at c, are equivalent to a point weighing W+Δ and lying on the straight line *cb* at a point c′, not far from c. The new position of rest is gained as soon as c′ lies vertically below the axis of rotation, or, to put it in other words, the right side of the beam goes down until the leverage of Δ is so far reduced and that of W has so far increased, that the two *momenta statica* are equal to each other.

Imagine now the axis of rotation were shifted vertically upwards through a small height *h*, but remained parallel to itself. The imaginary point weighing 2P now, as soon as the beam turns, *has* a lever and helps the weight W; the beam will turn through a less angle α' to gain its new position of rest, and, supposing 2P to increase, α' becomes less as 2P increases.

Imagine now the axis of rotation to be shifted downwards towards the centre of gravity. The heavy point weighing 2P grams now helps Δ, and the angle which separates the two positions of rest will become greater than the original angle; the greater 2P the greater will be the actual angle α''. But the two weights, W concentrated in c, and 2P concentrated in the centre of the line *ab*, taken jointly, are equivalent to one point c′ weighing W+2P grams, and situated on the straight line connecting the two points; and supposing 2P to increase gradually from *nil* onwards, c′, in the second case, will rise and rise, and at a certain value of 2P fall into the axis of rotation. The balance then has no definite position of rest; and if c′ rises still higher, the balance upsets. However small an overweight Δ may be put on either side, the beam would have to turn upside down to reach its one (theoretical) position of stable equilibrium.

The balance maker of course takes care so to adjust his instrument that even if the sensibility is at the highest value which the balance is meant to afford, and the two-sided charge 2P at its maximum likewise, the centre of gravity of the whole system lies on the safe side of the axis of rotation.

Assuming this condition to be fulfilled, the balance to be exactly equal armed and to be charged with a pan weighing p_0 grams and a load of *p* grams on each side, the angle α of deviation is governed by the equation

$$tg\alpha = \frac{\Delta l}{Ws + 2(p_0 + p)h}, \quad . \quad . \quad (1)$$

where *l* stands for the arm-length, *s* for the distance of the centre of gravity of the empty beam from the axis of rotation, and *h* for the distance of the axis of rotation from the plane of the two end-edges, the axis being assumed to lie *above* the plane. In the opposite case *h* must be assumed to be negative, or the *plus* sign before the second term in the denominator be replaced by a *minus* sign. But $tg\alpha$ is the ratio of the absolute length of scale (measured tangentially, *v. supra*) corresponding to angle α to the distance I of the tangent-zero from the axis of rotation. Hence we have

$$n = \frac{\Delta l\mathrm{I}}{Ws + 3(p_0 + p)h} = \Delta . \text{`E'} \quad . \quad (2)$$

where, supposing I to be measured in tangential scale degrees, *n* may be read as meaning the number of degrees through which the needle turns in consequence of the addition of Δ. The product condensed into 'E' we will call the 'sensibility.'

The reciprocal of E, *i.e.* the number $\mathrm{E}^{-1} = \frac{1}{\mathrm{E}}$, is the weight-value of 1 degree of the scale—*i.e.* the particular Δ which makes $n = 1$. With a precision balance the milligram is a convenient unit for Δ.

For a balance provided with the writer's auxiliary bob, eq. (2) may conveniently be brought into the form

$$\frac{\Delta}{n} = \mathrm{E}^{-1} = \frac{(Ws + 2\mathrm{P}h) + b(y_0 + y)}{l\mathrm{I}} \quad . \quad (2a)$$

where *b* is the weight of the bob and $y_0 + y$ the distance of its centre of gravity from the axis of rotation y_0, being that distance which prevails when the bob is at its highest (zero) position. In a well-made balance the influence of P on E is small; we may therefore assume the P of the equation to be some average value, and, contracting constants, say, the weight-value of one degree is

$$\mathrm{E}^{-1} = \mathrm{A} + \mathrm{B}y \quad . \quad . \quad (3)$$

where A and B are constants; A obviously being that value which E^{-1} assumes when $y = 0$. —B is easily determined by one trial at $y =$ to its maximum, and the scale thus standardised.

The theory of the rider might be allowed to take care of itself if in general practice the rider's path exactly coincided with the plane of the three axes. But such is not the case; this path, as a rule, lies above the plane, and each mark at its own altitude H. Let us therefore assume that, after the balance had been charged with P on each side, a rider weighing *p* had been suspended at a point of the beam corresponding to the fraction *kl* of the arm-length (at the $10k$)th mark counting from the centre). If the beam stand horizontal, and a weight *kp* be placed in the opposite pan, the beam will remain in equilibrium, because we have $l(pk) = p(kl)$ whatever H may be; the rider where it is and the charge *kp* (virtually) in the left knife-edge are conjointly equivalent to a fixed point weighing $kp + p$, and situated on the straight line joining the left edge and the point ($10k$) where the rider is. And this equivalence holds for the slanting beam as well, and is independent of P. But the sensibility of the beam with the rider on is evidently greater than it was with the rider off. Statically speaking, the weight of the beam and the two charges P and P are equivalent to a fixed point C_0 weighing $W'=W+2P$, and situated vertically below the axis of rotation at a distance S_0, and this particle, conjointly with the one embodied in the rider, is equivalent to a point weighing $W+2P+p$, and situated on the straight line between C_0 and the point where the rider sits. Referring to a system of rectangular co-ordinates whose X-axis passes through the centre of the central edge and is parallel to AB, and whose Y-axis passes through the same centre, we have for the position of the resultant point the equations

$$x(W'+p)=lkp\text{ ; and }y(W'+p)=W's_0-pH$$

$$\therefore\frac{x}{y}=tg\alpha=kp\left\{\frac{l}{W's_0-pH}\right\}\quad.\quad.\quad(4)$$

We see that if H be constant—*i.e.* if the rider-path be parallel to the plane of the three axes—$tg\alpha$ is proportional to the overweight kp virtually added to the charge of the right pan; but it is as well to notice that the $tg\alpha$ of our equation is different from the $(tg\alpha)_0$ which is brought about if, instead of hanging the rider on the $(10k)^{th}$ mark, we actually put kp units into the right pan. Obviously

$$(tg\alpha)_0=(kp)\frac{l}{W's_0}\text{ and less than }tg\alpha\quad.\quad(5)$$

With a rider weighing only 10 milligrams, and, say, a hectogram balance, the term pH in the denominator comes to very little, but with a rider of ten times the weight it (as a rule) can no longer be neglected; such a rider cannot conveniently be used unless H is constant and the rider must always hang at the balance (at its zero, over, say, the central knife when it is not used as a weight), or else the sensibility has one value with the heavy rider on and another with the rider off. Another requisite is that notches cut into the beam be substituted for mere marks, and that the rider have a sharp edge to give sufficient constancy of position to its point of application.

From what we have said so far, it would appear that in a balance provided with a gravity-bob we can give the sensibility any value we may fancy. And so we can, but it does not follow that we can command any desired degree of *precision*. Because the three edges and bearings are not what they ought to be, and, as a little reflection shows, the effect of their defects is the same as if, say, the length of the right arm, instead of being at the constant value l, oscillated irregularly between $l-\lambda$ and $l+\lambda$, where λ is a very small length, which increases when W and P increase, but is independent of l. And this again is the same as if λ were *nil*, but the charge of, say, the right side, instead of being at a constant value P, varied irregularly from $P-\epsilon$ to $P+\epsilon$. In a given balance charged with a given P at each side ϵ is constant, but the corresponding angle of deviation β varies when the sensibility varies. Within this angle β the balance is, so to say, in a state of indifferent equilibrium. By going a little more deeply into the matter, we easily satisfy ourselves that, even allowing for the fact that we cannot substitute a longer for a shorter beam without increasing the beam-weight, ϵ will increase when l becomes less. In a balance meant to afford a certain degree of precision, we cannot allow the arm length to fall below some (very uncertain) value of l_0.

A glance at eq. (2) would show, if it were not clear without it, that, if the three axes lie in exactly the same plane—*i.e.* if $h=0$—the sensibility becomes independent of the charge, which is a great convenience. But h obviously cannot be equal to *nil* at all charges; hence in the case of the best instruments it is regulated so that it has a small negative value when only the pans are suspended, and, by the unavoidable deflection of the beam, becomes *nil* at some suitably selected medium charge, so that, from this charge upwards, it has small positive values. That such a degree of precision cannot be attained by purely constructive methods goes without saying; indeed, any precision balance requires to be '*adjusted*' before it is fit to be used. For this purpose the value of the h corresponding to the medium charge and the ratio of the actual arm-lengths $l':l''$ must be determined and the errors h and $\frac{l'}{l''}-1$ corrected. For the direct geometric measurement of h special apparatus have been constructed, which, in their present form, we believe, afford a sufficient degree of precision; but the final test always is (or at least was until lately) at a suitable position of the bob, to determine the weight-value E^{-1} of one degree of deviation for a series of charges, say, $p=0$, 50, 100 grams, &c., up to the maximum charge which the balance is intended to measure; and to at least *virtually* calculate the corresponding values h by means of eq. (2). Whether h is positive or negative, is of course seen from the values E^{-1} without calculation. Supposing now h has a greater value than can be tolerated, one of the knives must be lowered or raised until at a certain medium charge the three edges are as exactly as possible in one plane. Most mechanicians provide adjusting screws for this purpose which enable one to work in a systematic manner. Some, however (for instance, Becker & Sons, following the example of Deleuil), prefer to fix all the knives definitely and to alter the *form of the beam itself* by means of the hammer. If the central edge has to be lowered, the lower bar of the beam is struck (on both sides); if it is to be raised, the upper bar is struck, until the correction is presumably almost but not quite completely effected. The values E^{-1} are then again determined, and if they are not sufficiently near one another, the hammering is renewed until the adjustment is perfect. In a similar manner (or by means of adjusting screws) the two arms are made equal to each other. The test here is very simple. The balance, after having been brought to the highest degree of sensibility which it will stand at the highest charge P, is charged with *exactly* P grams on each side. The longer arm goes down, and by determining the small overweight which must be added to the other side to establish equilibrium, we can easily determine the ratio $l':l''$ numerically. All these adjustments are effected by the mechanician, and when once effected are final. Some mechanicians—for instance, the Beckers—fix even the centre of gravity, but this is a mistake. A balance, to be complete, *must* have a movable 'bob' to enable the operator to give the sensibility that value which suits him best. What degree of sensibility should we choose? Answer: In general, the lowest degree which suffices for the purpose in hand. Supposing, for instance, we can neglect the half-milligram, it is of no use to screw up the bob any higher than necessary for rendering the angle of deviation corresponding to 0·5 milligram conveniently visible and no more, because the less the sensibility, the greater the range of weights determinable by the method of vibration, the greater, as is easily shown from eq. (2), the relative independence of the sensibility from the charge, and last, not least, the less the time of vibration. The time of vibration can of course not be allowed to fall below a certain minimum, or else the centres of gravity of the charges will not be able to follow the oscillations of the beam with sufficient promptitude. But this clause, with larger balances wrought at high precision, usually takes care of itself. The exact relation in a balance between the time of vibration t (in seconds) and the sensibility E is given by equation:

$$t^2 = \frac{l}{\mathrm{R1}}\left\{k\mathrm{W} + 2\mathrm{P}\right\}\cdot\mathrm{E} \quad . \quad . \quad (6)$$

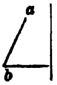
where R is the length of the mathematical pendulum beating seconds at the place of observation, P the total charge on one side, and k a numerical factor, $k\mathrm{W}l^2$ being the *momentum inertiæ* of the empty beam. With the customary perforated rhombus or triangle, k is very nearly equal to ⅓. From the equation we clearly see that with a 'bob' of sufficient range we can choose our own time of vibration or our own sensibility, but we cannot choose both, in a ready-made balance. It stands differently with a *balance to be constructed*. To avoid indefiniteness, let us assume that we wished to design a balance for weighing quantities up to 100 grams with a toleration of 0·1 mgr. Let us assume also that we had made up our minds regarding the material and the general form for the beam, and that we had defined the latter so that the relation between arm-length l, and weight W, were in accordance with an equation of the form

$$\mathrm{W} = \mathrm{C} + \mathrm{B}l \quad . \quad . \quad . \quad (7)$$

where W includes the empty pans, C designates the conjoint weight of all that which is independent of l; and B stands for the weight of the rest if the arm-length l=1. Our equation now assumes this form

$$t^2 = \frac{l}{\mathrm{R1}}\left\{\mathrm{C}^1 + 2p + bl\right\}\mathrm{E} \quad . \quad . \quad (8)$$

where p stands for the charge in each pan. This equation affords some guidance in the selection of l. Assuming for E a value which renders the decimilligram just visible, and taking p=0, we substitute for t the smallest admissible value and solve our equation in regard to l. Of course l cannot be allowed to fall below that minimum l_0 (*v. supra*) at which the inherent error would rise to anything like 0·1 mgr. Where does this limit value l_0 lie? Staudinger used to draw the line at 200, Oertling at 180 millimetres, and similar values were adopted by other makers, until Bunge, some twenty-five years ago, showed in the most direct manner possible that a sufficient degree of constancy can be attained with an arm-length of as little as 60 millimetres. Thanks to the general excellence of Bunge's work his short beams soon became very popular with chemists, and the fact that almost all other German makers have since come to adopt the Bunge system shows that the additional perfection in the pivots which the short beam undoubtedly demands is not so difficult to realise as an outsider might be inclined to think. *Assuming this difficulty to be overcome*, it cannot be denied that the short in opposition to the long beam does offer certain advantages. 1st. It is relatively light, and hence the working of the arrestment is a less effort. 2nd. It is less liable to irregularities through one-sided elevation or depression of temperature. Perhaps we may add that, 3rd, it is easier in its case than in that of the long beam to make a smooth-working arrestment, and on this account chiefly it enables one to weigh more quickly. 4th, and *least* in our opinion, it vibrates more quickly. Not that we value this last advantage at nothing. The writer's auxiliary bob indeed was invented with the very object of remedying the corresponding defect in the older form of the instrument, being originally intended to be used thus. In the outset, place the bob far down, say to the mark where 1° of deviation corresponds to 2 mgrs. or some other value securing great rapidity of vibration, and establish equilibrium as far as thus possible. Then raise the bob to the mark at which 1°=0·1 mgr., allow to vibrate, shift the rider correspondingly, and verify your result. The writer, however, soon came to find this method less convenient than he had expected, and adopted another very obvious expedient. It is easy in any beam to bring down the time of vibration to the least value one could reasonably wish for by screwing down the bob to the corresponding place. This, of course, may render the decimilligram invisible to the naked eye. But why not help the eye by optical means? An ordinary lens magnifying six times linearly affords more than there is any occasion for; only it magnifies the parallactic error as well, and the effort to avoid this error strains the eye very unpleasantly. This experience led the writer to the following combination, which he found to give perfect satisfaction. A narrow ivory scale divided into degrees of about 0·1 mm. is fixed slantingly to the needle pretty far down, yet far enough up for not obscuring the ordinary scale which does duty as usual; on the other hand, a compound microscope of feeble power, which passes through the central fixed portion of the front pane of the case, is fixed slantingly to the *pillar*. The microscope has one vertical 'wire' in its focus which acts as a needle. As the microscope inverts its images, the apparent motion of the wire in reference to the scale (which one easily persuades himself is fixed) is the same in sense as the real motion of the needle in reference to the ordinary scale, so that mistakes in regard to the + and − are avoided. The ordinary scale is graduated after the micro-scale so that each of its degrees is equal in angular value to 10° of the latter. The writer some five years ago caused Mr. Oertling to apply this arrangement to two of his balances, and he has found it to work very satisfactorily. Although it was originally intended chiefly for special occasions—the adjusting of weights, &c.—it is used even for our everyday work, as it was found that the microscope puts a less strain on the eye than the naked-eye reading of the ordinary scale. The microscopic arrangement described adds about 3*l.* to the cost of the balance. A cheaper arrangement is the following. A micro-scale, divided conveniently into fifth-millimetres, is fixed slantingly to the pillar, the needle at the corresponding part is shaped thus,



and a hair by means of capillary perforations is stretched out between *a* and *b*; the hair is parallel to the face of the scale, and only some 0·2 to 0·5 mm. removed from it. A short terrestrial telescope, fixed in the central (fixed) part of the front-pane of the case, serves for the readings. The object glass serves only to produce an image of the scale and hair within the tube, which the eye-piece (a compound microscope) magnifies as far as necessary. As the telescope need not be perfectly steady, it can be fixed at a relatively low cost. We have used this arrangement in connection with one of our balances for over two years, and found it to be almost as good as the one first described.

ON THE SETTING UP AND TESTING OF A PRECISION BALANCE.

A real precision balance, to be able to do justice to itself, must stand on a very steady support, in a room where it is not exposed to one-sided changes of temperature. The light should fall in from the back of the observer. The best support, of course, is a pillar of masonry, standing directly on the earth. Next after it (in a substantially built building) comes a shelf fixed to the wall by strong brackets. A good heavy table, however, suffices in practice. In a large city the street traffic becomes very inconvenient in weighing. Its effect can be minimised by putting small pieces of thick vulcanised-rubber plate between the legs of the case and the table. In the examination of a newly set-up balance we naturally begin by seeing that the arrestment, the rider-shifting apparatus, &c., are in good order, we then level the case, and next leave the balance to itself for some four hours at least, to enable it to acquire the temperature of the room. After these preliminaries we proceed to the following determinations.

Determination of the inherent error ϵ.—For this purpose we charge the balance equally on both sides with the highest weight which it is intended to measure (a hectogram balance, for instance, with a hundred-gram piece on each side), and after having established approximate equilibrium at the highest degree of sensibility which the balance will stand at this charge without giving obviously inconstant readings, determine the exact position of rest, first with the two hectograms in the centres of their pans, and then, in a series of successive experiments, with one or other of the hectograms placed at some point of the edge of its pan so as to give any non-parallelism in the axes or any other defect in the terminal pivots a good chance of influencing the result, taking care to interpolate occasionally an experiment with the two weights centrally placed in order to see if the balance still gives the same readings as it did at first. If it does not, this is probably owing to external causes, such as unequal heating of the two arms. To be able to translate degrees of deviation into differences of weight, we must at some stage make two successive determinations of the position of rest, one with P′ in the left and P″ in the right pan (P′ and P″ stand for the two hectogram-pieces) and another with, say, one milligram added to P″. For the precise determination of a position of rest, we cause the balance to vibrate moderately, and (neglecting the first reading as being in general liable to irregularities), record 3, 5, 7 . . . successive turning-points of the needle, applying a + to scale-points lying to the left, and a − to scale-points lying to the right of the zero (or *vice versâ*); an odd number in any case in order to correct for the retarding effect of the resistance of the air, &c.; those influences, in other words, through which the needle, supposing it to start from −4°, at the end of a double vibration, does not come back to exactly −4°, but perhaps to −3·7°. The algebraic sum of any two successive readings gives the point *a* of the scale at which the needle would come to rest, *in half-degrees*, and there is no reason why the half-degree should not be adopted as a convenient unit for the purpose in hand. Supposing the readings to be

$$\begin{array}{llllll} & a_1 & a_2 & a_3 & a_4 & a_5 \\ \text{(Example)} & +3{\cdot}7 & -2{\cdot}7 & +3{\cdot}5 & -2{\cdot}4 & +3{\cdot}5 \end{array}$$

we have for a the values: $a_1+a_2=+1{\cdot}0$; $a_2+a_3=+0{\cdot}8$; $a_3+a_4=+1{\cdot}1$; $a_4+a_5=+1{\cdot}1$—Mean $=+1{\cdot}0$.

The mean value of the four results is put down as *the* value of *a*. Supposing *a*, through the addition of Δ milligrams to the right charge to increase by *n* demi-degrees, then $E=\frac{n}{\Delta}$ (= 2 'E' in the sense of our equation (2)) is the sensibility in demi-degrees; and its reciprocal $E^{-1}=\frac{\Delta}{n}\left(=\frac{1}{2E}\ldots\text{ of equation (2)}\right)$ the weight-value of the demi-degree in milligrams. Supposing the values for *a* obtained with abnormal positions of the charges to be a_1, a_2, a_3, &c., instead of the mean value a_0, corresponding to the centrally placed charges, then $(a_0-a_1)E^{-1}=v_1$, $(a_0-a_2)E^{-1}=v_2$, &c., give each a value for the *inconstancy* of the balance in milligrams (or rather fractions of a milligram, it is to be hoped). According to a rule deduced from the law of frequency of error, the computation

$$r=\frac{0{\cdot}845}{\sqrt{n(n-1)}}(v_1+v_2+v_3+\ \ldots\ldots)$$

where all the *v*'s must be taken as positive, gives the 'probable' weight-value of the deviation of any one *a* from a_0, meaning that value of $(a_0-a)E^{-1}$ which, in a *very large number* of determinations, is as often exceeded as not reached. But in practice the number of determinations made is never sufficiently great to bring out anything like a close approximation to the law, and it suffices to take *r* as being equal to 0·845 times the mean of all the values *v*, and adopt it as sufficiently near to the theoretical 'ϵ.' The probability that, in a given case, $(a_0-a)E^{-1}$ *exceeds*

	$2r$	$3r$	$4r$	$5r$
is	0·18	0 04	0·007	0·0007

respectively.

In these determinations, if the balance lacks a microscopic reading arrangement, it is as well to read from a distance with a telescope, to avoid the parallactic error which we have no right to charge against the balance.

Determination of h.—All that is necessary is to determine the weight value of one degree in the sense of equation (2) for, say, $p=100$, 75, 50, 25, 0 grams, and to calculate the corresponding values h. In a good balance h is so small that (supposing our rule regarding the adjustment of the bob to be followed) the sensibility remains almost constant from $p=0$ to $p=100$ grams. Hence, practically, it suffices to adjust the bob so that at a convenient average charge (where 'average' refers to the most frequently occurring values of p) one demi-degree corresponds to say $\frac{1}{2}$ or $\frac{1}{4}$ of a milligram *exactly*, and then to see what it is at other charges. If there is no sufficient constancy we enter the values E^{-1} found on a system of rectangular co-ordinates in function of the charges p, and draw the nearest curve to the points. This curve (if h were absolutely constant) would be a straight line. In any case it supplies the data for a table of values for E^{-1}. This table, however, must not be relied on in *standard* weighings, because the value h is subject to changes, for this reason amongst others, that the agate of the knives has a different coefficient of expansion from the metal of the beam.

The arm-lengths.—For the determination of the ratio of the arm-lengths, the orthodox method (for a hectogram balance) is to adjust two hectogram-pieces to exact equality, and, after having established equilibrium, to put one into the left and the other into the right pan, &c. But in practice the following method is better. Take any two fairly well adjusted hectograms and viewing them, one as a *standard* representing 100,000, the other as an *object* weighing x milligrams, go through the ordinary operation of weighing once with the object in the left pan and the standard in the right, and once the other way.

Supposing (using S as a symbol for 100,000 milligrams) we find

$$xl' = (S+\delta_1)l'' \quad . \quad . \quad . \quad . \quad \text{I}$$

$$xl'' = (S+\delta_2)l' \quad . \quad . \quad . \quad . \quad \text{II}$$

(where any δ may be negative), we have by division of I by II, and subsequent multiplication with $l'' : l'$,

$$\left(\frac{l'}{l''}\right)^2 = \frac{S+\delta'}{S+\delta_2} = \frac{1+\frac{\delta_1}{S}}{1+\frac{\delta_2}{S}}$$

whence, as a sufficient approximation,

$$\frac{l'}{l''} = 1 + \frac{1}{2}\left(\frac{\delta_1-\delta_2}{S}\right)$$

No maker who has a name to lose would care to send out a precision balance in which $1-\frac{l''}{l'}$ is more than ±0·00005 at the outside, although for any scientific purpose a considerably greater error could be tolerated. The corresponding adjustment indeed, while of the first importance in commercial balances, in precision balances is in a sense irrelevant.

Unequal-armed Lever Balances.

(1) *The steelyard or Roman balance.*—In it only the shorter arm (of the length l) bears a pan; the longer arm, by notches cut into its back, is divided into parts of equal length, l being the unit. The working points or lines of the notches should lie in the plane of the two edges, being so many bearings for the knife-edge forming part of a sliding weight adjusted to P units. The unloaded balance is in its position of rest when the beam stands horizontal. To weigh a body, it is placed in the pan and the sliding weight shifted forwards from notch to notch until (when the weight hangs at the distance nl from the axis of rotation) the beam is again at rest in its horizontal position. We then have for the weight sought

$$xl = nlP \text{ or } x = nP.$$

As fully explained above, the principle of the steelyard is discounted in the modern precision balance for the determination of small differences of weight. In theory there is no objection to its extension to the determination of weights generally, but the technical difficulties to be overcome are great. On an equal-armed balance, whose beam is divided into 100 equal parts (from end to end), all weights from 0·0001 to 100 grams might be determined with three riders weighing half of (100, 1, and 0·01) gram respectively, but the realisation of 101 exact pivots is no small matter. Where relatively high precision is aimed at, it is better to provide only a small number of notches (say 10) and have a set of riders, weighing say 10, 1, 0·1, 0·01 grams respectively. The specific gravity balances of Westphal of Celle, are made on this principle. It strikes us that the steelyard principle might be discounted for the decimal subdivision of weights, thus:

Imagine a precision balance whose two arms measure $10l$ and $11l$ units. 10 grams placed in the pan of the longer arm are balanced by 10+1 grams placed in that of the shorter; hence a 1-gram piece may be adjusted after two exact 10-gram pieces, &c.

The tangent balance has only *one* short arm, from which the pan is suspended; its centre of gravity lies low, so that the *momentum staticum* Ws of the beam assumes a high value, and even a considerable weight placed in the pan produces only a moderate angle of deviation. The needle moves along a circular limb divided so that the readings are proportional to the tangents of the respective angles of deviation, and give the corresponding weights directly. The equation $\Delta = \frac{tg\alpha \cdot Ws}{l}$ (*see* equation (1), above) holds theoretically for any value Δ, but the angular deviation corresponding to 1 gram of additional charge becomes less and less as the charge increases. The tangent balance, though useful for the rough weighing of letters, parcels, &c., is not available for exact gravimetric work.

Compound Lever Balances.

In all these, practical convenience and rapid working are gained at the expense of precision. In the *Robertal balance* the pans are above the system of levers (which as a rule is concealed in a box), so that there is room for bodies of even large dimensions. Our diagram, Fig. 8, is intended to explain only the *principle* of the machine, which in practice assumes an endless variety of forms.

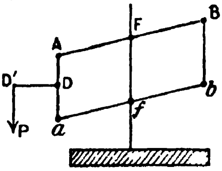


FIG. 8.

The beam consists of two parallel vertical parallelograms of which only the front one is represented in our figure. F and *f* (and F′ and *f′* in the other parallelogram) are fixed pivots, A, B, *a* and *b* (A′, B′, *a′*, *b′*, behind) are movable joints. On each side a horizontal bridge connects a point D on the vertical side A*a* (and a similar point on B*b*) with a corresponding point D′ on the back parallelogram (so that, for instance, A*a*, A′*a′*, DD′ form one piece) and, from the centres of these bridges, vertical rods arise which support the pans. Supposing each pan to be charged with P pounds, the centre of gravity of either of these two equal charges may lie in any of a great many positions about the respective pan, yet the statical effect is the same as if it were concentrated, one in the centre of the one bridge, and the other in the centre of the other; the two charges will balance each other, because, if the centre of gravity of one descends by *h* mm. that of the other rises by *h* mm., so that the work P*h* is the same on both sides. An over-weight added to one of the charges will bring down that side. The bars AB and A′B′ are relatively heavy beams, the lower bars *ab* and *a′b′* are light. Hence it depends chiefly on the distribution of the mass in the beams AB and A′B′ whether the balance (if nearly equally charged) has a definite position of rest: but even if it has, it will never vibrate like an ordinary balance, on account of the great friction in the numerous pivots. If it could only be cured of this defect, the Roberval would be the ideal balance for the counter or ordinary weighings in the laboratory. This problem has been to some extent solved in the torsion balance of Springer, in which the axes are realised in stretched out horizontal bands of elastic steel, which act, so to say, as knives and bearings in one.

The '*torsion balance*' is made[1] in a great variety of forms, but the principle of construction is the same in all. The following description is based upon the examination of what was sold as a high-class pair of counter-scales for loads up to 20 lbs. As shown by Fig. 9, the balance consists of two parallel beams united into a flexible parallelogram by means of three vertical frames, the bond of union in the case of each frame consisting of two horizontal bands of elastic steel, which bridge over certain gaps of the frames, the middle portion of each band being firmly united with the respective beam end at its lower side by means of a screwed-on block of metal. In this instrument the beams measure 290 mm. from end pivot to end pivot, the steel bands are 5·6 mm. broad and 0·49 mm. thick; the length of the working part of a band is 58 mm., 29 on each side of the beam. The middle band lies below the plane of the two end bands by about

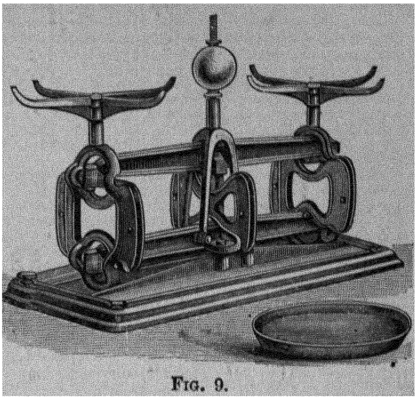


FIG. 9.

2 mm. The central frame, which does service as a pillar, is fixed to the sole of the instrument, the end frames are fixed only to their respective beam ends. Fig. 10, which is drawn to scale,

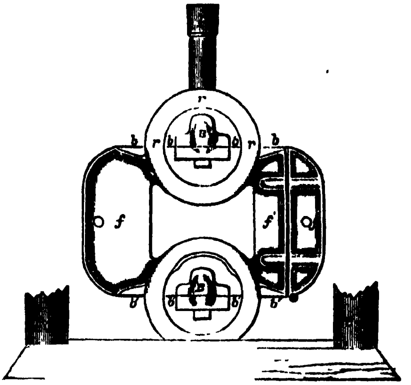


FIG. 10.

represents one of the end frames. The two steel bands of each frame, though independent of each other in their action, are really parts of one continuous band which is wound tightly round the edge of the frame, the ends meeting in B or B′, where they are, we presume, riveted on. To give them the requisite degree of high tension, the frame, of which part of the right side is movable, is stretched laterally (by means of pegs fixed to the two sides of a vice and slipped through the two holes of the frame) and the gap which is thus produced between the two halves of the right side of the frame is made permanent by means of metal plates wedged into it. The central frame is somewhat differently shaped from the lateral ones; the upper ring, *r*, is omitted, to enable the upper beam to pass freely through between the legs of a stool fixed to the lower and terminating in a vertical peg which serves as a needle and carries a globular gravity bob. The bob, which in the case of the balance under consideration weighs 458 grams, *i.e.* more than a pound, can be raised or lowered to enable the sensibility of the instrument to be varied. The system of beams is inclosed within a case of plate-glass; the top plate supports an arch made of a metal tube from which an ivory scale graduated on both sides is suspended vertically so that its lower edge runs through a notch in the upper sharpened end of the needle to enable the vibrations to be read from either side.

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[1] By the Torsion Balance and Scale Company, 92 Reade Street, New York.

To explain the working of the instrument, let us for a moment substitute for the steel bands so many linear wires, which, though unbendable, offer no resistance to torsional disfigurement. The torsion balance thus modified is in theory identical with the ideally perfect 'Roberval,' and, if the centres of gravity of the beams are in their axes of rotation, the parallelogram will be in a state of indifferent equilibrium at any shape which it may assume. To give it a definite position of rest, we must either shift (let us say one of) the centres of gravity vertically downwards, or else we must endow our ideal wires with torsional elasticity, which, of course, brings us back to the actual instrument. But the torsional elasticity of the steel bands is very considerably more than we want; its effect on the sensibility is the same as if (supposing the upper beam is suspended at its centre of gravity) that of the lower lay at a very considerable depth below its axis of rotation. To give the balance a sufficient degree of sensibility, we must raise the centre of gravity of say, the lower beam, until the stability of the position of rest is reduced to a sufficiently small value. In the actual instrument this is effected by means of the heavy gravity bob above referred to.

The principal advantage claimed for the torsion-balance, in contradistinction to the Roberval balance, is its freedom from friction; and this advantage it undoubtedly possesses, but it is compensated for to a large extent by the unavoidable viscosity in the elastic bands. The instrument described above, when equally charged on both sides, and with the bob sufficiently far down, vibrates like a precision balance of a high order; the position of rest as calculated from a series of couples of successive deviations of the needle, is remarkably constant up to at least a charge of 5 kilos. on each side; but once, when we determined the sensibility at first with no charge, then at a charge of 2 kilos., and lastly for a charge of 5 kilos., and then redetermined the sensibility of the unloaded instrument, we found that it was out of equilibrium to the extent of more than a decigram. We also found that the reading of the balance is not quite independent of the position of the loads on the pans.

The ordinary decimal balance, as used for weighing heavy loads, is a combination of levers as shown in Fig. 11. *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h*, are all joints or pivots; *a* and *h* rest on the fixed framework of the machine and consequently indirectly on the ground, *c* rests on the lever *ab*. In the actual machine *cd* supports the bridge which accommodates the load, while a pan suspended at *f* receives the weights. The pan is so adjusted that it counterpoises the bridge. Suppose the load amounts to P units and its centre of gravity lies vertically above *i*; a portion P_c presses on the knife-edge at *c* and the rest $P_d = P - P_c$ pulls at *d* and with the same force at *g*. Now P_c pulling at *c* is equivalent to a less force ${}_bP_c$ pulling at *b*, and ${}_bP_c \cdot ab = P_c \cdot ac$, whence ${}_bP_c = P_c\frac{ac}{ab}$. But ${}_bP_c$ pulling at *b* or *e* is equivalent to a greater force ${}_gP_c$ pulling at *g* and ${}_gP_c \cdot gh = {}_bP_c \cdot eh$; hence ${}_gP_c = \frac{eh}{gh} \cdot {}_bP_c = \frac{eh}{gh} \cdot \frac{ac}{ab} \cdot P_c$.

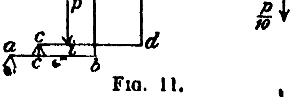

FIG. 11.

The dimensions are so adjusted that $\frac{eh}{gh} = \frac{ab}{ac}$ whence $\frac{eh}{gh} \cdot \frac{ac}{ab} = 1$; hence the joint effect of P_c and P_d at *g* is the same as if they both, *i.e.* P, were suspended at *g*; and if, for instance, *gh* is $\frac{1}{10}$ of *hf*, $\frac{1}{10}$ P units in the pan will balance the P units lying on the bridge. In many balances of this kind the long arm *hf* is divided so that lesser weights can be determined by means of a rider.

ELASTICITY BALANCES.

Imagine an elastic solid body—beam, wire, spiral, &c.—to be held fast in one or more fixed points, and suppose some one other point *a* to be used as a pivot for the suspension of a load of P units. Point *a* will sink until, at a certain depth *h*, the strain developed by the deformation of the working body balances that weight P. As long as the working body is not stretched beyond its limit of perfect elasticity, the length *h*, if not proportional to, is at least a fixed function of P; hence the path of *a* can be graduated, at least empirically, so that each point of the scale corresponds to a fixed number of units of weight. This is the general principle of the multitude of *spring balances*. Sometimes a relatively strong spring is used to effect only a small displacement of *a* even with the highest charge, but this displacement is then multiplied by a system of levers, so that the least difference of weight which the balance is meant to show becomes visible. In a very neat kind of spring-balance, which has become popular, the displacement of *a* is, by means of levers and a toothed wheel, translated into the circular motion of a needle which moves along a divided circular limb like the hands of a clock on their dial.

Jolly constructed a *quasi* precision spring-balance for sp gr. determinations thus:—A long spiral of wire is suspended vertically in front of a vertical millimetre-scale, etched on a strip of plate glass which is silvered behind, so as to avoid the error of parallax. From the lower end of the spiral a light pan is suspended; the index is close above the pan at a convenient point. The instrument has never come into general use, because any second-class precision balance beats it in every sense. A similar remark applies to an ingenious little instrument invented by Ritchie for the determination of minute weights.

Ritchie's balance consists of a very light beam whose axis of rotation passes through its centre of gravity, and which is firmly united with a thin horizontal wire which lies in the axis of rotation. The hind end of the wire is absolutely fixed to the stand; the front end forms the continuation of the axis of a circular pin revolvable within a circular bearing. A needle fixed radially to the pin points to a divided circular limb. The empty balance is so arranged before use that the beam when horizontal is at rest. To determine a small weight (x mgr.), it is placed in, say, the right pan, and the wire turned from the right to the left by turning the pin until after the needle has passed through a degrees (where a may be more than 360°); the beam is again at rest when horizontal. We then have x=const. a. The constant must be determined by experiments with known weights. Sartorius of Gottingen used to apply the Ritchie arrangement to his precision balances for the determination of differences of weight from 10 mgrs. downwards (Bibl. 5), but he has long since given up the notion: at any rate it is no longer to be seen in his price list. A Ritchie balance might perhaps do well for the adjusting of small weights, but a small precision steelyard would work infinitely better.

Sartorius' combination, if provided with a relatively strong wire, might make a handy instrument for the rapid (approximate) determination of weights without the use of any standard mass less than 1 gram.

The Hydrostatic Balance

is a hydrometer provided with a relatively large body and a narrow neck, and so adjusted that it weighs considerably less than its own volume of water. The top end of the neck bears a horizontal table, which serves as a pan, or, what is better, is provided with a horizontal system of cross-bars, from whose ends a pan is suspended by means of wires or chains, below the shelf supporting the vessel containing the floating hydrometer. A certain weight P, placed in the pan, brings down the hydrometer so far that the surface of the water touches a certain mark on the stem. If an unknown weight x requires to be supplemented by standard weights equal to p units, to produce the same effect, $x+p=\mathrm{P}$, or $x=\mathrm{P}-p$. Even for P= let us say 2 kilos., the neck need not be thicker than an ordinary knitting needle, so that the milligram, as a difference of weight, becomes perceptible. Wherever a precision balance has to be extemporised this instrument is useful; but it has no other *raison d'être.* Indeed of all the multitude of machines which the science of mechanics places at our disposal for the measurement of weights, the equal-armed lever-pendulum is the only one which, so far, has worked satisfactorily for precise gravimetric determinations.

A balance based on dynamical principles has been proposed. Imagine a pendulum provided with a shiftable bob above the fulcrum, and carrying a pan attached to the bottom end of the rod by a hook-and-eye. In a given instrument the time of vibration is a function of the distance of the bob from the fulcrum, and of the weight x of the object in the pan, and consequently the weight x is a function of the other variables.

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W. D.

On Highly Refined Weighing.

Introductory.—In the late Professor Dittmar's article (*vide supra*), typical forms of the precision and other balances have been considered: the theory of the balance and the conditions necessary for accurate work in general, have also been duly treated. In the present article, it is therefore unnecessary to add more than a consideration of some exceptional, but absolutely indispensable, precautionary measures adopted when we desire to reach that which some may be inclined to term an ultra-degree of refinement of weighing.

This article is based chiefly upon results obtained during two researches, which, for successful issue, demanded more than usual care. The subject was of necessity studied from the severely practical point of view; and few, if any, of the remarks that follow have their foundation in pure theory alone. The following points are severally discussed:—

(1) The Balance Room.
(2) The Balance Table.
(3) The Levelling Screws.
(4) The Scale.
(5) The Illumination of the Scale.
(6) Of possible Variations in the Level of the Bench.
(7) The Telescope and its Carriage.
(8) Of the Necessity for Fatiguing the Beam.
(9) Device for Maintaining Uniformity in the Temperature of the Beam.
(10) Temperature Coefficients of a Balance.
(11) Suppression of Air-Streams about the Pans.
(12) Concerning the Wiping of Glass Vessels.
(13) Of Certain Precautions to be taken in Weighing Glass Vessels.
(14) Determination of the Pressure Coefficients of Glass Globes.
(15) Of the Different Methods for Weighing.
(16) Errors attending the Weighing of Hot Bodies.

(1) *The Balance Room.*—The balance room should be upon the basement: and in selecting it, the choice should fall upon one having a north-easterly aspect: for then comparatively little

direct sunlight can enter the window even during midsummer. A dry, airy cellar is an almost ideal room for a balance that is to be used for highly refined weighing. But in either case, and particularly so in the latter, the variations in the temperature of the air within assume minimum values; this is frequently of great import. For a series of weighings, no weather is so favourable as that which prevails when the sky is overcast and wind absent.

(2) *The Balance Table.*—For work of supreme accuracy, it is imperative that the balance be placed upon a massive pillar of brickwork or stone: and this should rest upon a foundation sufficiently deep to guard against all local vibrations. The flooring should not have direct contact with the pillar; otherwise vibrations may readily pass from the former to the latter, and so to the balance. An excellent plan is to cap the pillar with a rectangular block of slate: this may have a thickness of from 1 to 1·5 inch. The slate should be closely cemented to the main block, and have its upper surface as far as possible truly plane. The slate, freed from all grit and dust, is covered either with a single fold of white linen or with white blotting-paper: and upon this is placed a sheet of thick plate glass, some 2 or 3 inches shorter and narrower than the slate. The paper or linen serves a twofold purpose: first, it acts as a necessary and convenient pad between the glass and slate; and, secondly, it secures for the worker a permanently white surface which renders even small objects sufficiently conspicuous. Near each corner two holes are drilled in the slate, for the reception of wooden pins having rubber covered heads. The positions of these are indicated in Fig. 12. The pins guard against any accidental displacement of the glass.

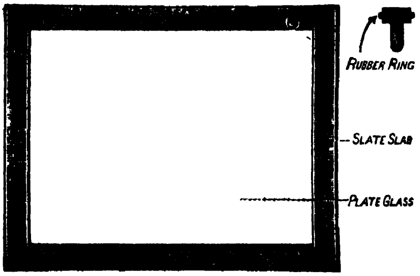

Fig. 12.

(3) *The Levelling Screws.*—With the above described bench, we may with advantage dispense with the brass shoes commonly employed for the levelling screws. When this course is adopted, the screws at their lower ends should terminate in highly polished spherical surfaces of low curvature. At those points where the screws have contact with the glass, a little oil is applied; medicinal paraffin oil is, on account of its non-liability to thicken, admirably suited for the purpose. The base of a balance thus mounted, readily adapts itself to modified conditions resulting from changes in temperature; and inherent stresses and strains are very little if at all affected.

(4) *The Scale.*—In some balances the scale divisions have an excessive length and breadth. Long lines produce an apparent narrowing of the contained spaces; and this increases the difficulty, already sufficiently great, of correctly estimating the turning position of the pointer. Again, a broad line is in general a very considerable fraction of a division; it is not easy to allow for this, and possibly the matter is sometimes overlooked. These two imperfections are reduced to insignificant proportions as follows:—

The slip of ivory is detached from the pillar, and the scale completely removed by lightly rubbing the ivory upon a very fine and large flat file; the slip is then re-polished, and a new scale in millimetres engraved upon it. The engraving tool must be capable of producing the finest of lines, and these are lightly drawn. The divisions, which may have a length of 1 mm., are rendered distinct by the momentary application of an etching pen charged with Indian ink. The ink readily runs along the whole line; occasionally a line may appear a little irregular; but after the ink has dried, any unevenness may be remedied by gently re-polishing with a flat pad. Fine sharp lines may often be secured by a *partial* filing down of the original scale, and the requisite shortness by a *complete* removal of the lower portions of the lines. During the process of shortening a straight-edge is used, not only as a guide for the file, but also as a protector for the portion of the scale to be retained.

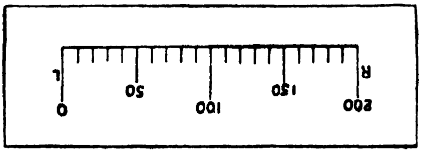

Fig. 13.

As the scale is invariably viewed through a telescope, which inverts the divisions and reverses their order, additional convenience is gained and possible confusion avoided by numbering principal lines as shown in Fig. 13.

(5) *The Illumination of the Scale.*—Weighings should be carried out in the absence of daylight; for unless the light from the window falls upon the balance in a perfectly symmetrical manner, and in general it is difficult to ensure this, the radiant energy absorbed by one part of the instrument will differ in quantity from that absorbed by another; this in itself would be immaterial, provided the ratios of the several quantities remained constant; but direct experimental evidence reveals fluctuations in these, and therefore corresponding variations in the zero or resting-point, R.P., of the beam follow. By using artificial light, we can eliminate this particular source of error. The following device leaves little to be desired:—

A glass globe having a capacity of some 10 or 12 litres, is filled with a dilute solution of potassium chromate and placed upon a shelf erected above the reading telescope. A glass tube, sealed at its lower end and containing an electric lamp, is placed centrally within the liquid: the light is then, by means of a large convex lens, concentrated upon the scale behind the pointer, and upon that alone. Ample illumination is thus secured; further, the light is practically free from heat rays, and owing to its monochromatic nature, the scale as seen through a correctly adjusted telescope is sharply defined. In Fig. 14, the relative positions of the telescope, lamp and lens are shown.

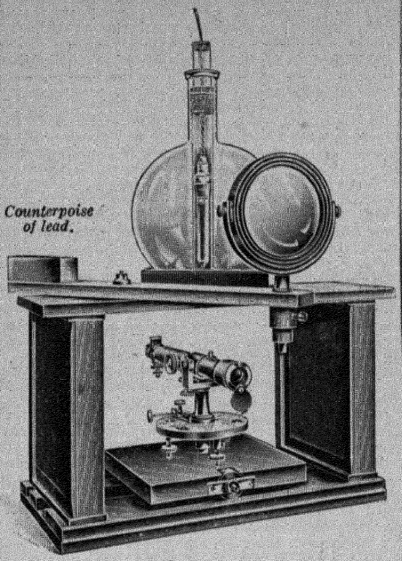

Fig. 14.

(6) *Of possible Variations in the Level of the Bench.*—An error which is readily overlooked, is that originating in variations in the level of the balance table. Observable changes may quickly follow a *sudden* rise or fall in the temperature of the room. Usually of a transitory nature, they are at times particularly noticeable and definite in a bench supported by wall brackets fixed above hot-water pipes. The variations are probably due to minute deformations resulting from inequalities of temperature. In connection with refined weighing, it is obvious that some plan must be adopted for detecting and measuring such variations. We have used with success the following simple form of tiltometer.

At one end of a glass tube T, Fig. 15, having a diameter of 3 cms. and a length of some 3 or 5 cms. greater than that of the balance pointer, a short capillary is formed; the other end is ground so that its containing plane is at right angles to the axis of the tube. Next, a short piece of platinum wire W_1, having a diameter of 0·5 mm., is, by means of gold, joined to one end of another platinum wire W_2, having a diameter of 0·05 mm., and a length some 3 cms. less than that of the tube; the free end of the fine wire is soldered to a small cylindrical weight Y, heavy enough to keep the wire taut; the resultant plumb-line is then introduced into the tube and the thicker wire fused into the capillary at the top. Any error in centring is remedied by a suitable bending of the wire W_1. A short scale, S, mounted upon a half-cylinder of boxwood, is fixed within the tube, so that its distance from the point of suspension of the fine wire equals the length of the balance pointer. The scale consists of 5 very small dots instead of lines; and the spaces they mark off are equal to the corresponding spaces of the scale behind the pointer; they are with advantage numbered and lettered according to the plan shown in Fig. 2. Vibrations of the plumb-line resulting from a necessary or accidental disturbance of the instrument, are quickly damped by oil in the vessel V. The tiltometer is completed by mounting the tube upon a rectangular base of thick plate glass; the width of this base is somewhat less than that of the balance case, but the length is some 3 or 4 inches greater. To the lower surface of the base are attached, by means of Canada balsam, 3 steel balls, and these are so disposed that when the instrument is *in situ*, each ball is in close proximity to a levelling screw of the balance. The position occupied by the tiltometer relatively to that of the balance, is shown in Fig. 16. When correctly adjusted, the scale

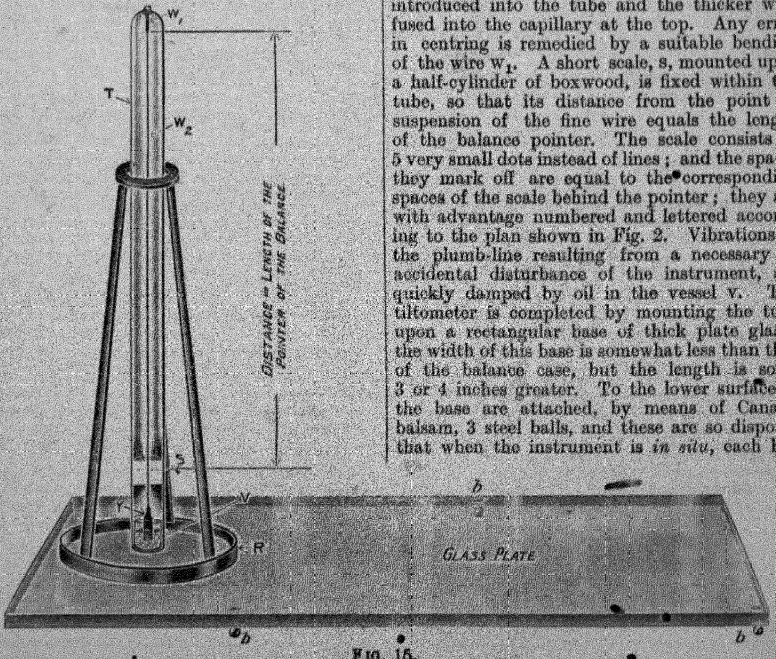

Fig. 15.

of the instrument and that of the balance pointer are in one and the same horizontal line, and they are contained by a vertical plane common to both.

With the tiltometer placed as indicated, it is evident that any vertical movements of the levelling screws resulting from a flexure of the bench, are also imparted, and in the same degree, to the tiltometer. Such movements, provided they are strictly equal, are not detrimental, and they pass undetected; but unequal flexures effect a change in level; and any appreciable change taking place along a line joining the two ends of the balance case, is recorded and may be measured by the tiltometer.

The tiltometer tube is protected by surrounding it with a metal guard, the base of which is a heavy brass ring R; this ring is prevented from being easily moved by smearing its under surface with resin cerate. The tube and its guard have no direct contact. For a series of weighings we proceed as follows:—

The telescope is first brought opposite the tiltometer and the position of the plumb-line determined with the aid of the micrometer. Next, the telescope is moved along until the scale behind the pointer appears in the field of view; the weighing is then carried out with all due precautions. Lastly, the tiltometer is re-observed: if the former and latter readings are identical, and they rarely differ within so short a time, the data for the weighing may be accepted; otherwise the experiment is rejected and a new one undertaken. When carrying out a new weighing at a later hour or on another day, the tiltometer reading may be slightly larger or smaller; but given an accurate knowledge of any such difference δ, the new weighing is easily reduced and made strictly comparable with the first, by the addition of ±δ to the second value obtained for the resting point, R.P., of the beam.

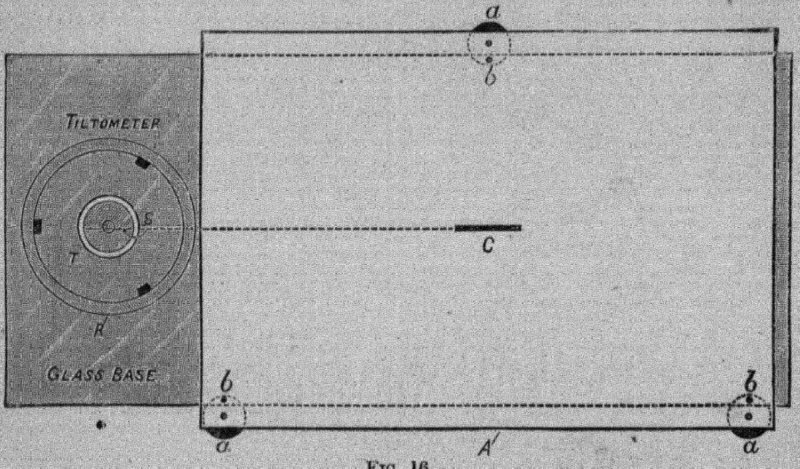

FIG. 16.

(7) *The Telescope and its Carriage.*—For observing the vibrations of the pointer, the best and most convenient plan is probably that in which the telescope is mounted upon a firm bench at a distance of approximately 2 metres from the balance. In order that the pointer as well as the tiltometer of the preceding paragraph may be readily and successively viewed, the telescope is placed upon a carriage having for its guide, a V-groove cut at right angles to the line of vision as shown in Fig. 17. The carriage has three supports; two consist of brass balls, which rest in the groove: one of those B is seen in the figure. The third support is a broad wheel W of boxwood. Easy and smooth movement is ensured by lubricating the groove with tallow. In order that the tiltometer (*vide supra*) may be read with accuracy, the eyepiece of the telescope is fitted with a horizontal micrometer M, graduated to 0·01 mm.

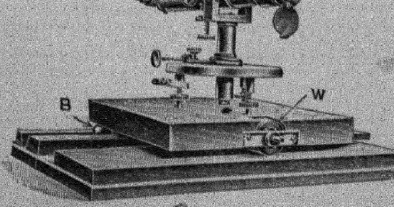

FIG. 17.

(8) *Of the Necessity for Fatiguing the Beam.*—Although from the practical point of view, a balance beam may in itself be perfectly inflexible, it is as yet impossible to so incorporate the knife edges that they and the beam shall constitute one absolutely rigid whole. On releasing a loaded beam, the consequent stresses bring about slight relative movements of the several knife edges and their screws. Such movements frequently affect, although in minute degree only, the ratio of the lengths of the balance arms. The time required for their

completion varies not only with the balance, but also with the load, and it may range from few to many minutes; but, in general, a period of from 10 to 15 minutes suffices. Now, from the above, it will be evident that no weighing can be of definite value, unless the knife edges have already assumed truly normal positions; and in order that they may do so, the balance must be *fatigued*. This simple operation consists in allowing the beam to vibrate, for an appropriate time, after the pans have been loaded and the weights adjusted for weighing; the beam is perfectly fatigued when successive R.P. determinations agree. Having reduced the balance to a normal state, the actual weighing is undertaken; and for this the crank handle is first cautiously turned, so that without in any way relieving the instrument of its load, one of the arrestors is momentarily and very gently made to lift its pan and thus cause the beam to re-oscillate. Several vibrations having passed unrecorded, the usual observations for the determination of the R.P. are carried out. The above remarks concerning fatiguing, are equally applicable in the case of an 'unloaded' balance. In Fig. 18 we have an illustration typical in character and magnitude, of initial knife-edge movements. The curve there shown, and in which successive R.Ps. are graphed against corresponding time intervals, represents the results of an experiment with a highly inflexible beam of the cantilever form. The movements, at first of an oscillatory nature, die away, and finally the R.P. acquires a constant value.

If for any reason the loaded beam is arrested, the balance must again be fatigued before a final weighing is proceeded with. When it is necessary to readjust the position of the rider upon the fatigued beam, the operation may be carried out without detriment, by first slowly raising the pan arrestors until they are in such a position that, although they do not support the loaded pans and so relieve the beam, they reduce the vibrations to a very small amplitude.

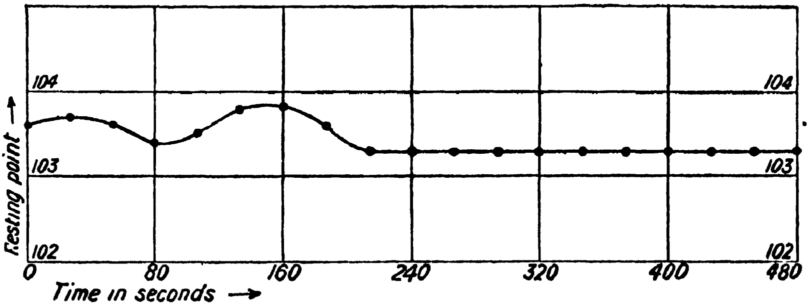

FIG. 18.

(9) *Device for maintaining Uniformity in the Temperature of the Beam.*—If a differential bolometer is arranged within a balance case, so that its two resistance coils are separated by a distance equal, say, to the length of the beam, it is easy to show that small and rapid fluctuations in the temperature of the air are continually taking place, even when the case is closed. On lifting the shutter, the fluctuations become more marked, and during the loading of the pans they are, comparatively speaking, quite violent. A pair of sensitive mercury-in-glass thermometers similarly placed, naturally fail, on account of their sluggishness, to indicate variations in temperature; they show a mean value only. In order that the highest degree of precision may be attained, it is imperative that the temperature of the air enveloping the beam should remain for at least some time, both before and during the process of weighing, strictly uniform. The required uniformity may be ensured by the device illustrated in Fig. 19.

As may be seen, we have here, in addition to the usual balance case, a small inner auxiliary chamber which completely encloses the beam. The base plate *c*, *d*, of this chamber, is of aluminium, having a thickness of 2 mm. or more; it is suitably slotted and perforated for the passage of the pointer and hooks by which the pans are suspended. The ends E, F, are conveniently made of well-seasoned mahogany, having a thickness of 1 cm. The front, back and also the top of the chamber, are of 8–10 mm. thick plate glass. The front of the chamber may be removed and the beam thus rendered accessible, after dropping the holders *h*, *k*. Discs *r*, *s*, *t*, of thin aluminium, are fastened to the pointer and pan hooks a little below the base

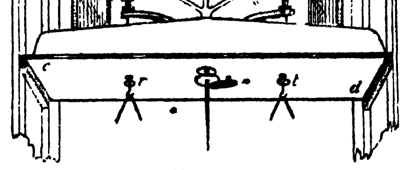

FIG. 19.

plate; these screen the apertures immediately above them. When placed within the auxiliary chamber, a differential bolometer recording variations as small as $\frac{1}{5000}$° C. remains quite unaffected, even during the loading of the pans. The decided advantage held by the protected over the unprotected beam is very well shown in Fig. 20. The groups *a*, *b* are the bolometer records obtained when, using 9 weights, one of the pans was loaded and unloaded six times in succession. During the experiments, the position of the bolometer near the beam remained unchanged.[1]

(10) *Temperature Coefficients of a Balance.*—Other conditions being constant, the R.P. of a beam will, in general, vary simultaneously with the temperature; therefore, unless the balance is thermostatically controlled, we must know with considerable exactitude the *temperature coefficient k* of the instrument. The value of *k* will vary with the balance and also with its load; but for a given balance, the several values of *k* for different loads may be determined as follows:—

Commencing at an early hour, when presumably the temperature of the room is at its lowest, and with the pans as the only load, the beam is released and duly fatigued; the R.P. is then found and the thermometer in close proximity to the beam read. Using hot-water pipes, an electric radiator, or a gas-fire, the temperature of the room is next raised by about 2° C.; a little later the R.P. is re-determined and the thermometer within the balance case read a second time. Proceeding in this way step by step, a total range of temperature of some 10° or 12° C. is covered. Finally, the room is allowed to reassume its original temperature, or approximately so, and a last determination of the R.P. for this series made. If the first and last members of the series are in agreement, the R.P. values for the higher temperatures should be reliable. From the data thus obtained, a temperature coefficient curve is now prepared by plotting the R.P. values against those for the corresponding temperatures; the resultant graph enables us to discover the true R.P. for any temperature falling within the experimental limits and for the particular load employed. (In this case, the so-called zero load.) Extrapolation should never be resorted to; for *k* may at any other temperature assume a distinctly different value; its sign may even be reversed: and so *k*, from being an additive, may become a subtractive quantity. Usually, it will be sufficient if the temperature of the beam is known to 0·05° C. The thermometer is placed horizontally within the auxiliary case.

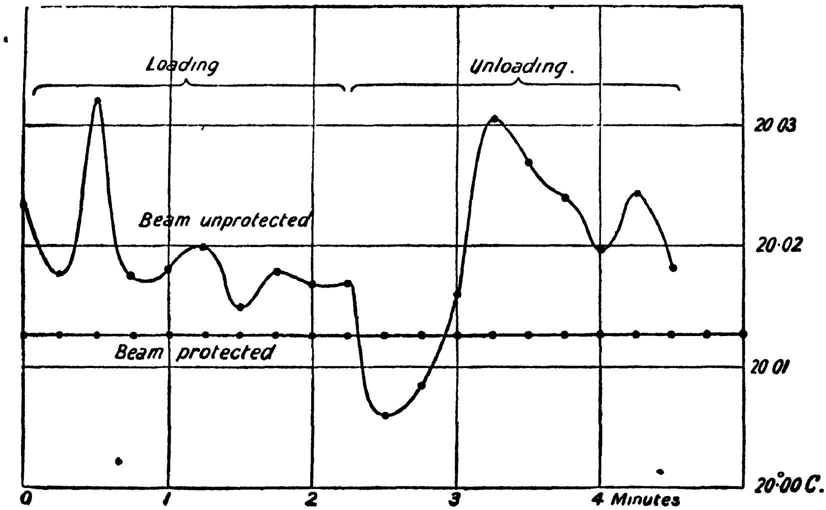

FIG. 20.

With the completion of the above, further operations identical in kind are proceeded with; and unless the balance develops abnormal behaviour, experiments with four additional loads will suffice. For a 200-grm. balance, the several loads may conveniently be 50, 100, 150, and 200 grms. The results obtained with each of these loads are, as before, represented by smoothed graphs, all drawn upon one and the same sheet. Often these graphs are of the same family; with such a group we may, for the given range of temperature, make use of interpolated values for drawing the temperature coefficient curve corresponding to an intermediate load. Finally, the whole series is completed by a re-determination of the R.Ps. for the unloaded pans: the value of all the results is thereby greatly enhanced.

Characteristic curves for *k* for a 200-grm. balance are reproduced in Fig. 21. The two dotted line curves were derived from interpolated values.

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[1] An excellent plan is to permanently set up a differential bolometer in the immediate vicinity of the beam; the thermometric condition of the enveloping air can then be readily tested at any time.

(11) *The Suppression of Air-streams about the Pans*—Increased accuracy is secured and labour saved, by adopting some plan whereby uniformity in the temperature of the air surrounding the pans is ensured; one that in practice has proved highly efficient is illustrated in Fig. 22.

Each pan, together with its stirrup, is enclosed by a fixed and massive brass cylinder C, having a diameter but little greater than that of the pan. The cylinders extend from the floor of the balance case, where they fit into grooves in thick brass plates PP, to the aluminium plate of the auxiliary chamber; and each is surrounded by a slightly larger cylinder B, which rests upon 3 wheels attached to C; these wheels, of which four lettered W are shown, are placed apart at an angle of 120°. By covering that portion of the fixed cylinder enclosed by B with silk, a smooth and easy movement is imparted to the latter when the handle H is pressed towards the right or left. To render the pans accessible, large rectangular apertures A are cut in the cylinders; these are opened or closed by an appropriate rotation of B. In the figure, the left-hand cylinder is open and the other closed. The interior surfaces of the cylinders are coated with a dead-black lacquer, but the exterior surfaces are polished and left unvarnished. Now, theory and practice alike show that with these conditions, a temperature uniform in the highest degree, and one, moreover, unsusceptible to any but slow variations, is quickly established. But given uniformity in temperature, it follows that within a space so limited and confined, winds or air-streams are non-existent; and therefore the minor irregularities ordinarily arising from convection currents about the pans, are avoided.

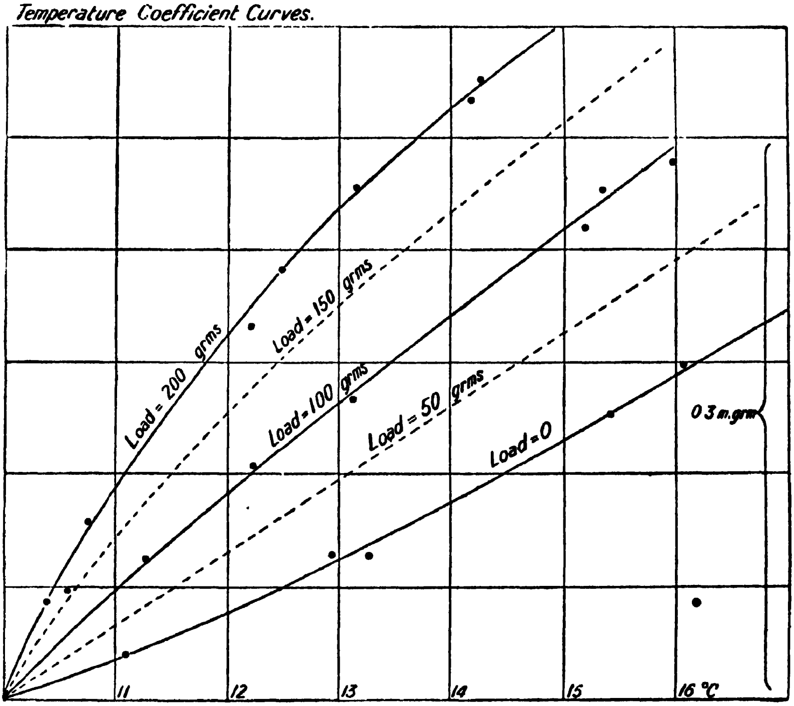

FIG. 21.

(12) *Concerning the Wiping of Glass Vessels.*—For glass vessels that are to be weighed with any degree of refinement, a most careful wiping is an indispensable preliminary; and in making choice of material for the purpose, some discrimination must be shown. Theoretical considerations verified by experiment, lead to the conclusion that in all probability it would be difficult to discover anything superior or equal to silk; this substance possesses a very low heat conductivity; and during use good specimens show a remarkably small tendency for casting off loose filaments. Objection is sometimes taken to the production of electric charges; but from the practical point of view, the ground upon which the objection is based is more imaginary than real.

During the process of wiping, direct contact between the vessel and the hand must be scrupulously avoided; more particularly so if we desire to maintain constancy of temperature. Some four or even more folds of silk should intervene between the hand and the vessel; and if at the same time the hands are thickly gloved, so much the better. The vessel immediately after it has been wiped, should be transferred to the pan of the balance with the aid of a suitable lifter. When the temperature of a globe having a capacity of 200 c.c. is raised by $\frac{1}{10}$° C., the consequent loss in buoyancy results in an apparent increase of weight equal to $\frac{1}{10}$ mg. A slightly warmed vessel reassumes its original temperature with extreme slowness; hence the desirability for guarding against any change in its temperature.

(13) *Of the Precautions to be taken in weighing Glass Vessels.*—In weighing glass vessels, sealed or open, special difficulties are encountered. These chiefly arise from (1) the variableness of the water skin upon the surface; (2) the fluctuating temperature and pressure of the air; and (3) in the case of closed vessels, the inconstancy of volume resulting from changes in the temperature and effective pressure within; the difficulties are still further accentuated when the vessel contains liquid matter, and more particularly so when the contents are solid. For many purposes the errors attendant upon causes (1) and (2) are sufficiently compensated by counterpoising the experimental vessels with others having very similar volumes; but some cases demand additional precautionary measures. Such measures are called for when, from the nature of the investigation, equality of *area* as well as that of volume becomes a prime necessity. Now, although two volumes may, by trial, be adjusted to almost strict equality, to secure at the same time a similar equality of area is a highly difficult problem; and yet, unless conditions are so ordered that a complete absence of moisture is ensured, a difference in the areas of a vessel and its counterpoise may well prove fatal to the object in view. This particular difficulty is surmounted in the following way:—

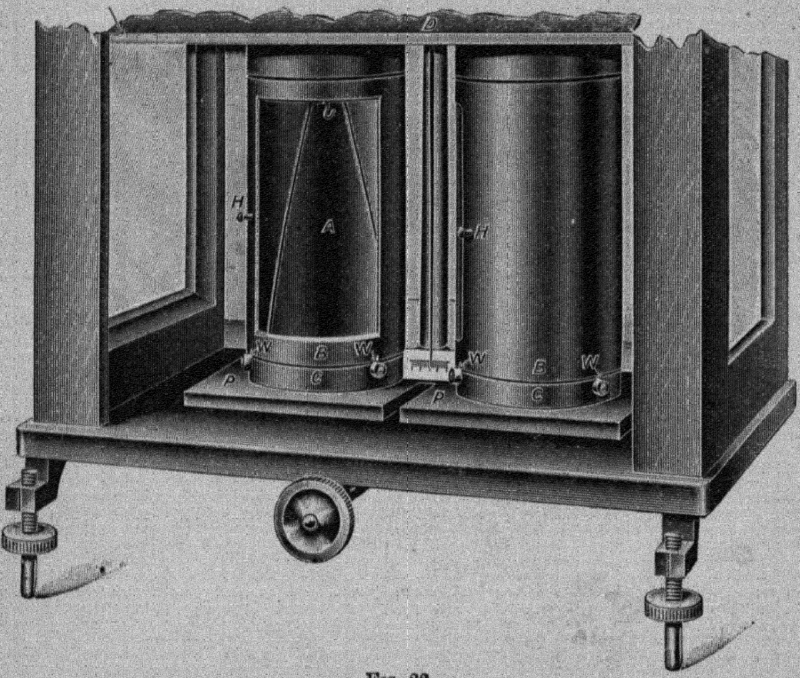

FIG. 22.

A blower is formed by fitting up a large glass jar A, as shown in the self-explanatory Fig. 23. A slow working of the Bunsen water pump *p* is all that is required for keeping the jar full of air, the pressure of which is governed by the length of the tube supporting the bulb R. On leaving the jar by way of the tap *t*, the air is by means of two further taps divided into equal streams; each stream is driven first through a Drecshel wash-bottle, and then through a spiral glass tube, both charged with concentrated sulphuric acid. The stream on emerging from the spiral, enters its own set of 3 purifying tubes; the first half of each set is packed with small fragments of soda-lime, and the second half with similar pieces of calcium chloride. Finally, the air is filtered through glass wool or asbestos, and led, first through the walls of the balance case, and then through the upper ends of the cylinders surrounding the pans. From thence either stream is delivered through a glass jet directed downwards and placed centrally within its cylinder. With the above described apparatus, any two objects (*e.g.* a closed vessel and its counterpoise), whose masses are to be subsequently compared, can be simultaneously subjected to a very perfect washing with air freed from carbon dioxide, moisture, and dust; this washing is allowed to proceed during the fatiguing of the beam. On escaping from the cylinders, the purified air displaces the ordinary air of the balance case; and as it is unnecessary to re-open the shutter before weighing, the operation is carried out within an atmosphere of standard and easily reproducible quality. A great convenience is secured if the air streams can be arrested by taps placed near the balance; these taps are closed just before the object is weighed. The plan here advocated has met with favour in several of the Oxford laboratories, where it has now been used for some years. The method might with advantage be universally substituted for the defective plan so commonly adopted with chemical and physical balances. To do this for any balance, it is but necessary to pass tubes delivering purified air, through the top of the case just above the pans or in a line with the extremities of the beam. The usual method for drying the air within a balance case has several serious objections, which cannot be discussed here.

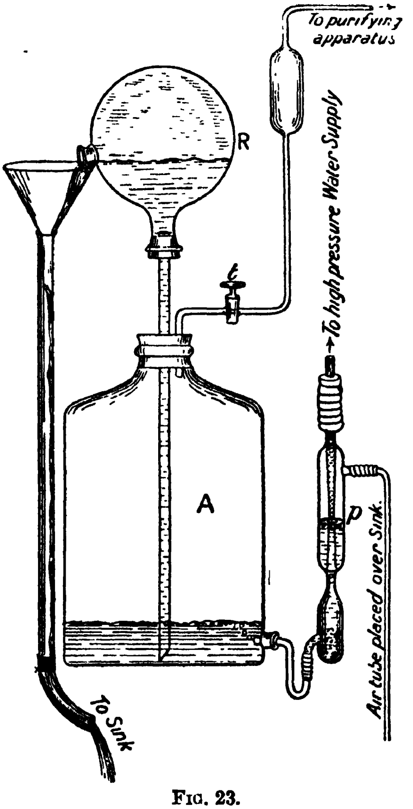

FIG. 23.

(14). *Determination of the Pressure Coefficients of Glass Globes.*—When closed vessels are weighed under different pressures, it is important that the vessel and its counterpoise possess not only similarity of form and volume, but also walls of equal thickness, otherwise compensation may be imperfect and vary with the pressure.

The pressure coefficients of expansion of globular vessels may be compared and accurately measured with the aid of the apparatus indicated in Fig. 24. The taps having been temporarily removed, either globe is introduced into the bell jar A, and its neck passed up through an airtight cork securely fixed in the mouth of the jar; a glass tap, connected with a sealed mercury manometer *m*, is then fused at *d* to the neck of the globe, and the open end of the jar closed by a stout brass plate *p*; the plate may be attached with Faraday cement or marine glue, both of which are insoluble in water and readily soften with heat. Next, through a hole in the cork made for the reception of the tube T, air-free water is introduced until the jar is completely filled; the tube T, also filled with water, is then placed *in situ*, and its fine capillary jet kept immersed in water as shown.

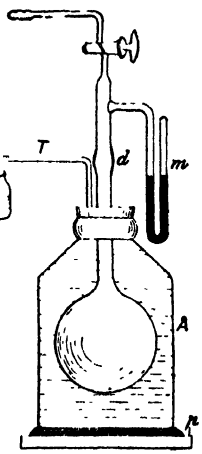

FIG. 24.

In measuring the pressure coefficient, a small weighed bottle is first substituted for that usually kept beneath the jet; air is then forced into the globe until the desired pressure is indicated by the manometer; as the pressure distends the globe, water is ejected into the bottle; this is weighed and the expansion resulting from the pressure calculated. If a series of pressures be applied, their values may subsequently be plotted against the corresponding expansions; from the graph thus obtained expansions for other pressures are readily determined. With slight and obvious modifications contraction coefficients may also be measured.

(15). *Of the Apparent Change in the Weight of a Cooling Body.*—When it is necessary to heat a body before its weight is determined, ample time must be allowed for the subsequent cooling. The time required for a hot body to assume the temperature of the balance case is greater than one would in general suppose. The importance of delaying the weighing until the object has acquired the temperature of the surrounding air is admirably illustrated in the following Fig. 25.

The data for the above graph was obtained as follows: A No. 00 B.P. crucible was heated to bright redness for some time and then removed from the flame. When the crucible was no longer *visibly* hot, it was placed upon the balance and immediately weighed under ordinary conditions; this weighing was followed by others at convenient intervals until 9 weighings in all had been carried out. During the period of half an hour required for the experiment, the weight of the crucible was constantly growing, at first rapidly, and then slowly; and notwithstanding the smallness of the mass, its limited surface and the free cooling in air, the apparent weight of the crucible had not attained a maximum value when the experiment was terminated. The observed changes in the apparent weight result from a summation of various effects of which the following appear to be the chief.

1. An apparent *increase* in weight due to (α) the gradual re-condensation of moisture upon the glazed surface; (β) a slight increase in the length of the arm supporting the object pan; (γ) the re-absorption of air and moisture by the porous mass of the crucible; and (δ) the lessened buoyancy of the heated air immediately enveloping the crucible and balance pan.

2. An apparent *decrease* in weight due to ascending convection currents which tend to lift the object pan.

The lengthening of the balance arm noted in 1 (β) is effected by the heated air rising from the cooling crucible. The re-absorption of air and moisture (1, (β)) by the general mass of the porcelain was rendered possible by the entire absence of glaze upon the bottom of the crucible. When the crucible is completely glazed, the internal condition of the porcelain remains presumably for all practical purposes, strictly constant.

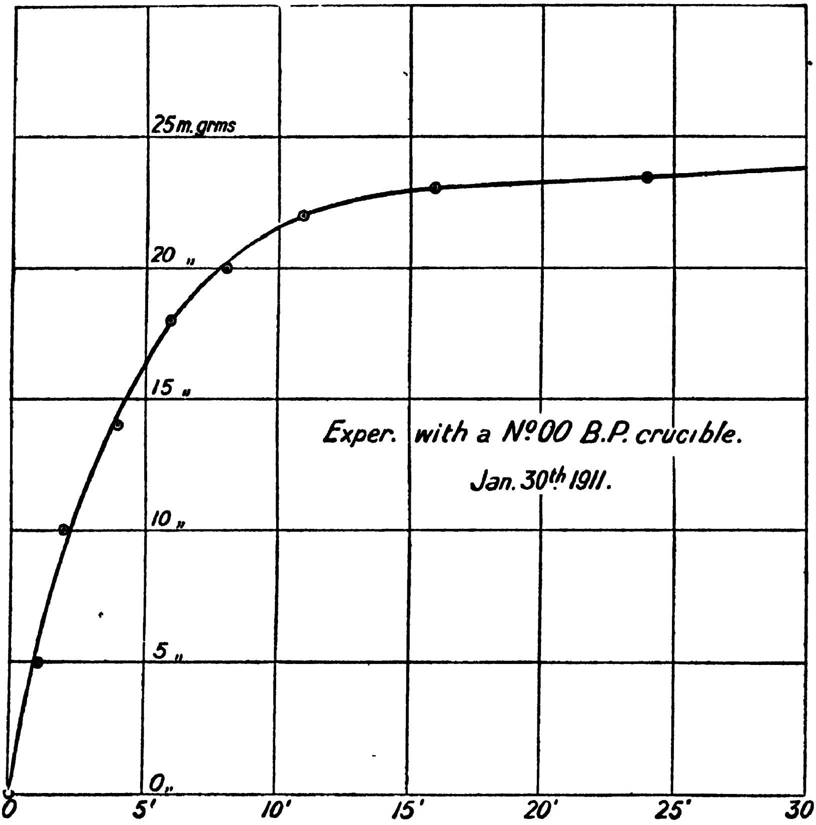

FIG. 25.

(16) *Concerning Ordinary Balance Cases.*—(*a*) With few exceptions the top of the usual balance case consists of a sunk glass panel *a*, *b* (Fig. 26); this is a constructional defect which we remedy in the following way. A strip of velvet *p* about an inch wide is fastened by means of thin glue or seccotine along the four sides and near the edges of the top of the balance case, as shown in the accompanying Fig. 26.

When the glue has hardened, but not before, a piece of plate glass AB, sufficiently large to just overlap the rectangle is placed upon the velvet. The velvet surface not only grips the glass and thus prevents it from being readily disturbed, but also acts as a highly efficient filter and so prevents dust from penetrating to the ordinary panel within. The added panel is easily dusted, and during the cleaning we do not as before incur the risk of forcing dust between the glass and the supporting surfaces and so to the interior of the balance case.

(β) The case of a precision balance should be opened or closed by sliding rather than by hinged doors. When a hinged door is opened the pressure of the air within the case is momentarily lowered; in consequence of this, the external air rushes through the innumerable crevices in the framework, and sweeping before it the erstwhile quiescent dust, charges the space within with floating particles. This fact may be verified by conducting an experiment in bright sunlight; on opening the door the sunbeams at once reveal the incoming dust.

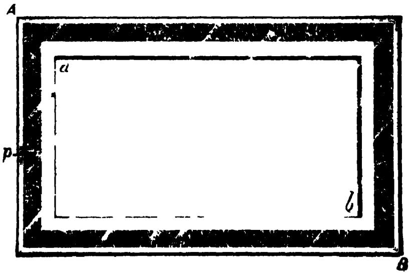

Fig. 26.

(γ) All sliding doors should run with great smoothness, and they should be fitted with counterpoising weights after the manner of ordinary window sashes. Shutters that are arrested by clutches are highly objectionable. During the working of a clutch vibrations are set up, and these are communicated to the balance with detrimental effects.

(17) *Of the Different Methods of Weighing.*—An article on weighing is incomplete unless it contains some allusion to the several methods available for accurate work; but those methods are so well known both in theory and practice that the briefest outline will here suffice. To begin with, we take it as granted that an experimenter seeking for high precision would use the method of vibrations for ascertaining the R.P. of his balance; in the preceding article this matter has been dealt with by the late Prof. Dittmar; and, therefore, further comment would appear uncalled for. Secondly, apart from the common differential method used by chemists and physicists for much of their work, there remain (1) the method of Borda, and (2) that introduced by Gauss.

(1) In Borda's method the object to be weighed is placed in either pan, and then accurately counterpoised by any convenient unknown masses; such masses may consist of indifferent brass weights, lead shots, fine sand, &c. When the adjustment is complete, standard masses are substituted for the object, and these are varied until equilibrium has been re-established. Given unchanging conditions, it is obvious that the total weight of the standard masses equals the sought-for weight of the body. To this method may be opposed the two objections: (α), its tediousness and (β) the impossibility of adjusting two initially different magnitudes to *precise* equality. These objections are so weighty that Borda's method is, comparatively speaking, but seldom used.

(2) Following Gauss and using the method of vibrations, the R.P. is found with the object first in one pan and then in the other; two determinations, d_1, d_2, of the R.P. are thus obtained. Then if S be the sensibility of the balance in mg., the ***difference*** D between the weight of the standard mass employed and that of the object is given by the equation

$$D = \pm \frac{d_1 - d_2}{2} . S \text{ mg.}$$

and the apparent weight of the body is thus determined. The superiority of this method over others is based upon a principle well understood by physicists, that in general it is easier to determine with accuracy by how much two magnitudes differ than to discover the true value of either.

For some further information upon the very important subject of highly refined weighing, the reader may be referred to (1) 'The Limitations of the Balance,' B. Blount, Chem. Soc. Trans. 1917, vol. cxi. 1035, (2) 'Vacuum Balance Cases,' Blount and Woodcock, Chem. Soc. Trans. 1918, vol. cxiii. 81; (3) 'Observations on the Anomalous Behaviour of Delicate Balances,' Manley, Phil. Trans. Series A, vol. ccx. 387-415; (4) 'On the Apparent Change in Weight during Chemical Reaction,' Manley, Phil. Trans. Series A, vol. ccxii. 227-260; (5) 'Observed Variations in the Temperature Coefficients of a Precision Balance,' Manley, Proc. Roy. Soc. A, vol. lxxxvi. 591-600; and (6) 'Dependence of Gravity on Temperature,' Southerns, Proc. Roy. Soc. A, vol. lxxviii. 393. As the above third-named paper contains references to other papers bearing upon the same subject, it is unnecessary to repeat them here.

In concluding this particular branch of an interesting subject, we may state that by availing ourselves of all precautions at present known to us, it has been found possible to attain the accuracy of ± 1 in 2 × 10^8 or thereabouts.

Micro-balances.—For the accurate determination of extremely small masses, instruments known as *micro-balances* are used. These are of two types; the action of the one depends upon torsion, and that of the other upon gravity; but of the two the latter has been the more successfully and highly developed. Nernst and Riesenfeld (Ber. 1903, 36, 2086) described a torsion balance sensitive to 0·0005 mg. with a load of several milligrams (for applications of same, *v.* Jänecke, Zeitsch. anal. Chem. 1904, 43, 547; Brill, Ber. 1905, 38, 140; Brill and Evans, Chem. Soc. Trans. 1908, 93, 1442). The zero of this balance is inconstant, and its sensitiveness varies greatly with the load. Gravity balances have been made by Steele and Grant (Proc. Roy. Soc. 1909, A. 82, 580), and modified by Gray and Ramsay (*ibid.* 1911, A. 84, 536; 1912, A. 86, 270), to carry loads ranging from 1 or 2 mg. to 1 decigram with a sensitiveness of 1×10^{-7} to 4×10^{-9} grm. The zeros of these balances remain constant over long periods of time.

The beam, consisting of thin silica rods fused together to form a framework as shown in Fig. 27, has a length of 10 cms (in Fig. 28 (*a*) a beam having a more rigid type is represented). The quartz knife edge rests upon a highly polished and truly plane quartz surface secured to the top of the brass pillar B

The vibrations of the balance are observed by means of a beam of light introduced through the window C and reflected by a tiny platinised quartz mirror fused to the beam at D; with the mirror in this position, its angular movements are not accompanied by appreciable ones of a translational kind. The reflected light falls upon a vertical mm. scale placed at some convenient distance from the mirror. The three-way tap E allows the interior of the balance case to be put into communication with either the atmosphere or a vacuum pump; the manometer F records the pressure within the case. A fine quartz thread fused to the beam at G supports (i.) a quartz bulb H of known volume V c.c. (either filled with air or vacuous), (ii.) the scale-pan J, and (iii.) a quartz counterpoise K. The whole hangs within the tube L (fitted to the case by the ground glass joint M), and is counterpoised by a solid bead of silica fused to the beam at N. A little uranium oxide inside the case ionises the air and eliminates disturbing electrical effects; and calcium chloride in L keeps the interior dry.

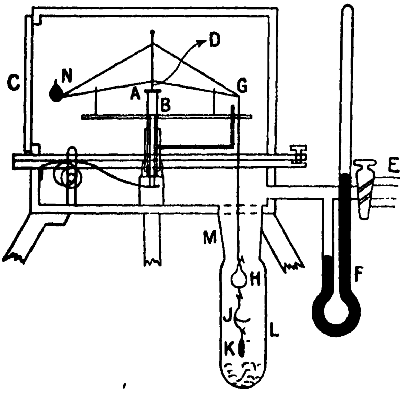

FIG. 27.

To perform a weighing, the pressure in the case is suitably lowered (to P_1 at temp. T_1 abs.), and the position of the reflected spot of light on the scale taken as the zero. The substance is then placed on the pan J, and a new pressure (P_2 at temp. T_2 abs.) determined under which the zero of the balance is recovered. The weight of the substance is then given by the expression (σ_0 = wt. of 1 c.c. air at N.T.P.)

$$\frac{273V\sigma_0}{760}\left(\frac{P_2}{T_2}-\frac{P_1}{T_1}\right)$$

The usual vacuum correction is, of course, necessary. Only weights less than the weight of air that the bulb can hold may be thus determined. To measure greater weights, the counterpoise K is replaced by a lighter one; a series of such counterpoises is required, and the differences between their weights may be measured on the micro-balance itself. It is convenient to make the bead N counterpoise the bulb, scale pan, and a set of weights (Fig. 28 (*b*)) (ranging from 2 to 0·1 mgm. and made from capillary quartz tubing: these are calibrated on the balance). In weighing a substance, weights are removed to obtain a coarse adjustment; the pressure within the case is then altered, thereby making the (variable) buoyancy of the air on the bulb H effect the fine adjustment. The absolute accuracy of the weighings is limited to the accuracy with which V may be determined; their relative accuracy is much greater.

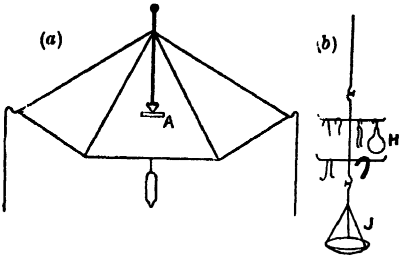

FIG. 28.

In a balance constructed by Steele and Grant, the beam, &c. weighed 0·93 grm., the bulb H had a capacity of 0·422 c.c. and contained $5{\cdot}04\times10^{-4}$ grms. of air; the balance had a period of 33 secs., and was sensivitive to 4×10^{-8} grm.

The micro-balance of Gray and Ramsay has been modified by Hans Pettersson (Göteborgs, Vet. Vitterh. Samf. 1914, 14th series, xvi). In the altered form the central knife edges are dispensed with, and the beam suspended, as shown in Fig 29, by two thin quartz fibres, which are highly attenuated at their points of junction with the horizontal rod. Pettersson also greatly improved the balance case; and for a vacuum-tight cement he uses an alloy having a low fusing-point. Further, the beam arrestment is magnetically controlled through the top of the balance case; in this way, certain sources of error, due to possible air leakage, are avoided.

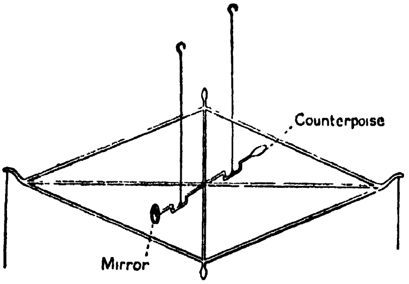

FIG. 29.

R. Strömberg (Annalen, der Physik. 1915, 47, 939), has improved the Pettersson balance, and at the same time increased its sensibility by the substitution of detachable for fixed threads. The form of the Strömberg suspension is shown in Fig. 30, and the complete Pettersson-Strömberg beam and its accessories in Fig. 31. To the axial rod of the balance are attached (1) a tiny screw

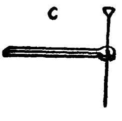

FIG. 30.

, for adjusting the centre of gravity, and (2) a minute plane mirror *m*, for indicating with the aid of reflected light the angular position of the beam. A section of the complete balance is shown in Fig. 32. An instrument of this type when carrying its maximum load of 50 mg., may apparently have a sensibility as high as ·01 μ-mgrm. (1×10^{-11} grm.). The Pettersson-Strömberg balance has been used for testing the validity of Poynting's law at high temperatures, for measuring the volatility of silica at 800° C., and also for the accurate determination of the diamagnetic constants of gaseous hydrogen and nitrogen.

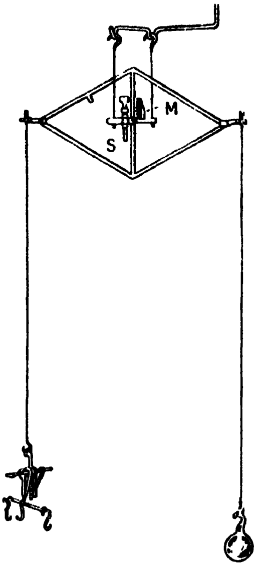

FIG. 31.

A simple form of micro-balance for determining the density of a gas has been described by F. W. Aston (Proc. Roy. Soc. 1914, A. 89, 439). The balance, which is made entirely of quartz, is represented in Fig. 33. The beam consists of two thin rods fused together as shown; the lower end of the shorter rod, *k*, terminates in a knife edge which rests upon a quartz plane. To one end of the beam is fused a bulb *b*, having a capacity of about 0·3 c.c., and to the other the counterpoising rod *r*. The case, made of rectangular pieces of plate glass, is as diminutive as circumstances permit; the cell containing the beam is not more than 3 mm. wide, and its volume is a few c.c. only. A special chamber *c*, which is cemented to the left end of the case, is closed by the stopper *s*, which is pushed in until it just fails to touch the contained bulb. One limb of a T-tube having a capillary bore, gives access to the interior of the balance case; the second limb is fused to a mercury manometer, and the third to a 3-way tap. By means of this tap communication between the balance

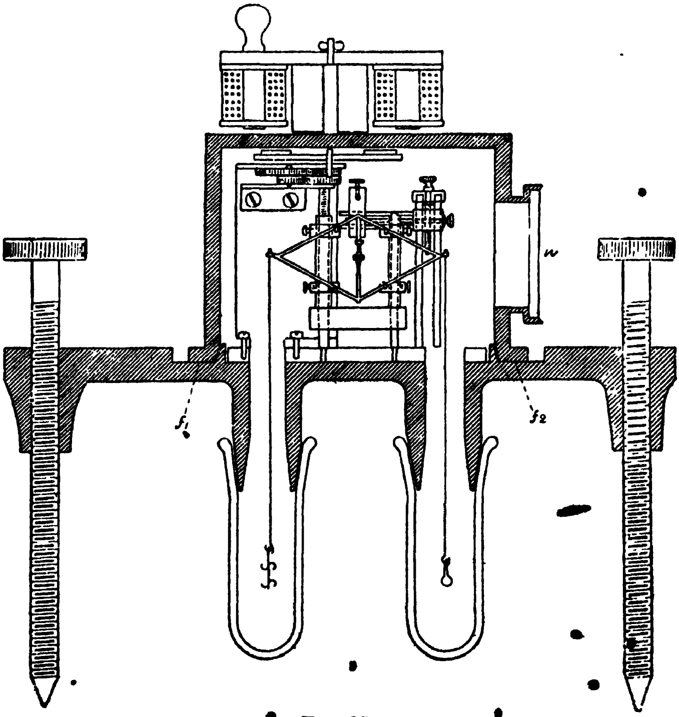

FIG. 32.

and an air-pump or the gas-admission apparatus can be established. With the above described apparatus the density of a gas is usually determined at a pressure of about 100 mm. of mercury Measured at N.T.P., the volume of gas actually required for an experiment is approximately 0·5 c.c. A density determination is carried out as follows: The balance case is first highly

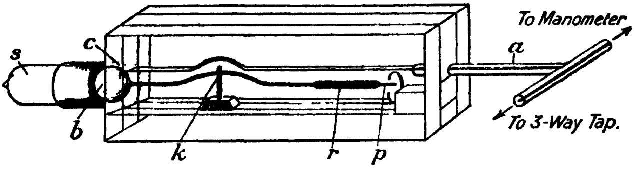

FIG. 33.

exhausted, then the gas of which the density is sought is admitted until the bulb rises and the point *p* of the counterpoise appears in the field of a fixed reading microscope. The pressure is then varied until the beam comes to rest at some convenient but quite arbitrary zero, and the manometer read. Finally, the case is re-exhausted and the experiment repeated with a gas of known density. The ratio of the densities of the two gases is equal to the inverse ratio of the corresponding pressures The determination can be made in a few minutes, and with an accuracy of from 0·1 to 0 01 p.c. For accurate measurements Aston's micro-balance needs, no less than the heavier precision instrument (*vide supra*), a preliminary fatiguing. This operation appears to be best carried out by maintaining for some days a high vacuum within the balance case.

Riesenfeld and Möller (Zeitsch. Electrochem. 1915, 21, 131) describe a form of micro-balance for which they claim a sensibility of $3{\cdot}3 \times 10^{-8}$ grm., when the balance is carrying its maximum load of 5 mg. The beam is a glass capillary tube 13 cms. long; this is supported by a quartz thread attached at a point 3 cms. from one end. A mirror, made from a quarter of a microscope cover glass, is secured to the end of the shorter arm, and from the other end of the beam the pan is suspended. Various ways of supporting the pan are described, but the most successful for high sensitiveness is that obtained by fastening a quartz thread horizontally and at right angles to the end of the arm. From this is hung the quartz thread which carries the pan. The arrestment consists of a clamp of two feathers, placed near the end of the longer arm.

Kramer (Chem. Zeit. 1917, 41, 773) has constructed a micro-balance of the usual type, with a carrying capacity of 1 grm. The length of the beam is 154·4 mm., and the weight 7·825 grm. When the balance is unloaded the sensibility is equal to 48 divisions per 0·1 mg, this decreases to 35 divisions for a load of 100 mg., and to 10 divisions for a load of 1000 mgr. A division equals 0 35 mm

The *micro-assay balance*, known in Germany as a 'Mikro-Chemische Wagen.' is a chemical balance in miniature, it stands as it were midway between the high grade chemical balance of precision and the true micro-balance of Steele and Grant and others. The beam, which may have a carrying capacity of from 1 to 20 grms., is rigid and exceptionally light; some of the more modern beams are also extremely short. First-class instruments have a high sensibility, and when lightly loaded the beam will usually indicate differences in weight ranging, according to the sensibility of the balance, from ·05 to ·005 mg.

Fig. 34 represents a highly sensitive micro-assay balance by Kuhlmann of Hamburg. The beam, which is 7 cms. long, is built to carry a maximum load of 20 grms. in each pan. The sensibility is such that each scale division corresponds to ·01 mg.; and by a special device for reading tenths of a scale division, differences in weight as small as ·001 mg. can be observed.

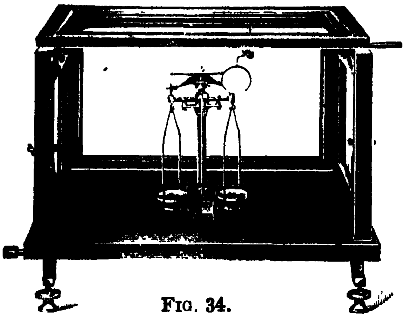

FIG. 34.

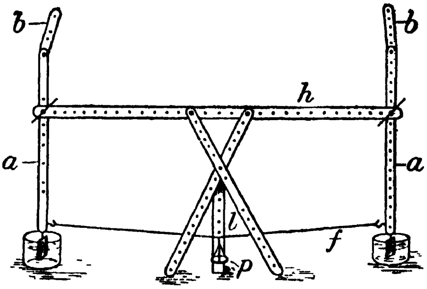

FIG. 35.

It may be unnecessary to add that the remarks and suggestions that have been made in connection with the heavier balance of precision are equally applicable to the assay balance.

A simple form of micro-balance for use in bacteriological laboratories, has been described by Shaxby (Proc. Phys. Soc. of London, 1919, 32, 21. The instrument is for loads varying from 0·005 to 0·5 grm.; its sensibility and 'dead-beat' character are such that weighings may be carried out rapidly and with an accuracy of from one to two parts per thousand. The balance (Fig. 35), constructed of 'Meccano' strips, consists essentially of three parts: (1) a tripod of which the hinder leg *l* terminates in a small flat foot which can be fastened to the table by means of a drawing-pin; (2) a horizontal strip *h* 2 feet long secured to the top of the tripod; and (3) a pair of compound vertical arms each consisting of a 25-hole strip *a* to the upper end of which is bolted a 6-hole strip *b*; each arm is suspended at a point just above its centre of gravity by means of a silk thread *f* passing through a glass tube T (Fig. 36), having rounded edges and a length of ¼ inch; the ends of the thread are held as shown by wire pins *pp*. The required 'dead-beat' action is obtained by immersing the aluminium vanes with which the arms are provided in water (Figs. 35 and 37). The balance is completed by linking the arms together with a fibre *f* (Figs. 35 and 37) of unspun silk from the central point of which is suspended a paper pan *p* for receiving the objects to be weighed. For weighing slips of paper before and after the absorption of a liquid, an aluminium clip *c* (Fig. 38) is substituted for the pan shown in Fig. 35. The balance is adjusted by varying the inclination of the strips *bb* (Fig. 35); and by the same means the tension of the thread and therefore the sensibility of the instrument can be altered. Before use the balance must be calibrated; and this is done by placing in the pan, each in turn, a series of five weights equal to one-fifth, two-fifths, &c., of the maximum load, and noting the resulting depressions of the central point of the fibre *f* with the aid of a vertical mm. scale placed behind it: the requisite precautions are, of course, taken to avoid parallax in reading. Weight values are now plotted against corresponding depressions and a smooth curve termed a *weight curve* drawn. To determine an unknown weight the object is placed in the pan or clip and the resulting depression read: this being known the weight with the aid of the graph can be ascertained. J. J. M.

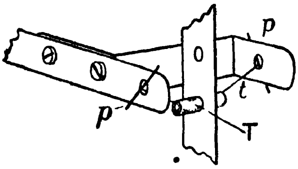

FIG. 36.

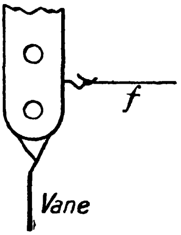

FIG. 37.

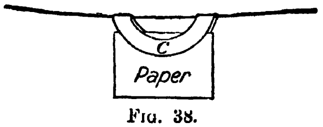

FIG. 38.

BALANOPHORE WAX *v.* WAXES.

BALATA is the product obtained by coagulating the latex of *Mimusops globosa*, Gaertn., a large forest tree, belonging to the natural order Sapotaceæ, which is a native of British, Dutch, and French Guiana, Venezuela, Trinidad, Jamaica, and probably Brazil north of the Amazon. In British Guiana and the West Indies the tree is known as the 'bullet' or 'bully' tree.

In physical properties and chemical composition, balata resembles true guttapercha, for which it is the best natural substitute, and it is of interest in this connection that the tree yielding it belongs to the same order as the trees (*Palaquium* spp.) which furnish guttapercha.

The balata trees are tapped by making a series of incisions in the bark, so arranged that the latex can run down to the base of the trunk, where it is collected in a calabash. The latex is afterwards poured into shallow wooden vessels, which are usually greased or rubbed with soap to prevent the balata from adhering to them, and allowed to stand exposed to the air until it has coagulated spontaneously; a sheet of balata is thus formed, which, when sufficiently hard, is removed from the vessel and hung up to dry. The coagulation of the latex may also be brought about by boiling, in which case the balata is obtained in the form of 'block.' Formerly it was the custom to fell the trees and then to cut rings in the bark in order to obtain the latex, but this practice, which involves the destruction of the trees, is now prevented as far as possible.

The latex of balata trees usually flows freely, and, in favourable circumstances, the yield from a tree 15–20 inches in diameter, tapped to a height of 8 feet, is about 3 pints, representing from 1½ to 2 lb. of dry balata.

Commercial balata may be either grey, pinkish or brown. When immersed in hot water it behaves like guttapercha, becoming soft and plastic, and, on cooling, it slowly hardens again without becoming brittle.

Balata is also similar to guttapercha (*q.v.*) in chemical composition, consisting essentially of a hydrocarbon (*gutta*), of empirical formula $C_{10}H_{16}$, associated with resins; the commercial product also includes varying amounts of insoluble matter (dirt) and moisture. Balata contains a much higher proportion of resins than good guttapercha, and is therefore inferior in quality to the latter; when compared with

guttapercha containing a similar amount of resin, it is found to be a little softer and more flexible.

The composition of Balata is shown by the following typical analyses:—

Description.	Source.	Moisture per cent.	Gutta per cent.	Resin per cent.	Proteid per cent.	Dirt per cent.	Ash per cent.
Specially prepared sheet [1]	British Guiana	1·9	49·7	44·0	3·8	nil	0·6
Block balata [1] . .	Venezuela	1·8	45·7	44·2	3·0	5·3	[1·28]
Commercial specimens [2,3]	Mostly British Guiana	13·8	41·5	34·8	—	9·9	—
Balata [2]	Dutch Guiana	5·3	43·5	36·9	—	14·3	—

The gutta of balata is very tenacious and of excellent quality; it is insoluble in alcohol, acetone, ether, or cold petroleum spirit, but is readily dissolved by chloroform, carbon disulphide, or boiling petroleum spirit. The resins present are similar to those of guttapercha, and consist of (1) a white crystalline resin (*albane*) soluble in hot but insoluble in cold alcohol; and (2) an amorphous yellow resin (*fluavile*) soluble in cold alcohol. An examination of the total resin of balata by Obach showed that it consisted of about 2 parts of albane to 3 parts of fluavile.

Balata is utilised commercially as a substitute for guttapercha. Its chief applications are for the manufacture of belting, in which the balata is interposed between layers of canvas; for insulating purposes; and for the manufacture of the covers of golf balls, after the removal of the greater part of the resin by solvents. It is also employed to a considerable extent for mixing with rubber, and for numerous minor purposes.

The bulk of the commercial supplies of balata are obtained from British and Dutch Guiana and Venezuela. *Cf.* Ter Laag, Caout. et Guttaperclia, 1915, 12, 8610. H. B.

BALLISTITE *v.* EXPLOSIVES.

BALLOON or FLEXIBLE VARNISH *v.* VARNISH.

BALL SODA *v.* SODA MANUFACTURE, art. *Sodium.*

BALM OF COPAIBA *v.* OLEO-RESINS.

BALM OF GILEAD. *Mecca* or *Opobalsam* (*v.* OLEO-RESINS).

BALSAMS. The exudations of plants, whether spontaneous or promoted by incisions made in their stems or roots, consist chiefly of resin, gum, volatile oil, and certain aromatic acids, or mixtures of these. The *resins* are characterised by insolubility in water and solubility in alcohol, the *gums* by solubility in water and insolubility in alcohol, and both by not being volatile without decomposition. In certain exudations the resin is dissolved in volatile oil, forming the class of *oleo-resins* of which the so-called Canada balsam is an instance. Gum arabic is a familiar instance of a gum obtained direct from the plant; mastic is an instance of a resin. The class of *gum-resins* may be represented by myrrh.

Now, amongst these resins and oleo-resins there is a group the members of which are marked by possessing a peculiar fragrant odour and agreeable pungent taste, which is due to the presence of free or combined cinnamic or benzoic acid. These are the *balsams*, and it is convenient to consider them as a class by themselves. The word 'balsam,' it is true, has sometimes been used in a wider sense—indeed, it was originally employed for an oleo-resin resembling the so-called Canada balsam; but it is more convenient to restrict the term to resins or oleo-resins which contain cinnamic or benzoic acid. The balsams have long been familiar to writers on materia medica, some of them being known to Pliny, and even earlier to the Greek physicians. They are favourite constituents of the incense used in the Greek and Roman churches, and while they cannot be said to have an important therapeutic value, they are reputed mild tonics and stimulants and are a common flavouring agent in expectorant medicines. The following are the more important:—

Benzoin. *Gum Benjamin*; *Benzoïnum*, B.P., U.S.P. (*Benzoin*, Fr.; *Benzoëharz*, Ger.). The benzoïn of Java and Sumatra is derived from the thick-stemmed trees of *Styrax Benzoin* (Dryander, Phil. Trans. 1787, 303; Bentl. a. Trim. 169), while the more highly prized Siam benzoïn is probably obtained, according to Royle, from the *Styrax Finlaysoniana* (Wall). The source of Siam benzoïn is, however, still uncertain (Holmes, Pharm. J. [3] 14, 354). The first European writer to mention benzoïn is Batuta, who travelled in the East early in the fourteenth century, and from that time to the present day the drug has been an established article of materia medica. It is largely used for incense and in the preparation of fumigating pastilles, and enters into the well-known Friars' Balsam or compound tincture of benzoïn, a favourite dressing for wounds.

The juice exudes from the trees as the result of incisions, and it is allowed to harden before it is removed. During the first three years of the life of a tree the balsam dries in the form of *tears*. This is called *head* benzoïn, and is the most highly reputed. A less esteemed variety is obtained during the following seven or eight years, which is browner in colour and is called *belly* benzoïn. Lastly, the trees are split, and the commoner *foot* benzoïn is scraped off (*cf.* Flück. a. Hanb. 405).

Benzoïn is obtained as a hard brittle mass, consisting essentially of a mixture of resins together with uncombined benzoic and sometimes cinnamic acids. The resins are entirely soluble in solution of potash and in alcohol, but by their behaviour toward other solvents they have been distinguished as *a-resin*, *β-resin*, &c. (Unverdorben, Pogg. Ann. 8, 397; Kopp, Compt. rend. 19, 1269; Van der Vliet, Annalen, 34, 177). The yield of *benzoic acid* varies from 12 to 20 p.c., being on an average about 14 p.c.

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[1] Analysed at Imperial Institute.

[2] Analysed by Dr. Obach.

[3] Average figures for nineteen commercial lots representing 50 tons.

To extract it (1) the benzoïn may be mixed with sand and heated in a suitable vessel, over which is placed a receiver to collect the vapours of benzoic acid, which condense in beautiful tufts of acicular crystals: or (2) the benzoïn may be boiled with milk of lime, filtered, and after concentration of the calcium benzoate solution thus obtained, the benzoic acid precipitated by hydrochloric acid: or (3) the free benzoic acid may be extracted by treating the powdered resin with warm carbon disulphide. Lüdy (Arch. Pharm. 231, 43) has shown that the α-, β-, and γ- resins of the earlier investigators are mixtures of the partially hydrolysed cinnamates of the resin alcohols present, the α-resin being the least and the γ- the most hydrolysed. He also finds that benzoïn from Sumatra contains *benzoic acid*, *styrene*, traces of *benzaldehyde* and *benzene*, 1 p.c. of *vanillin*, 1 p.c. of *phenylpropyl cinnamate*, 2–3 p.c. of *cinnamyl cinnamate*, and a mixture of a little *benzoresinol cinnamate* with much *resinotannol cinnamate*, this mixture forming the main constituent of the balsam. In addition, woody impurities occur to the extent of 14–17 p.c., also free *cinnamic acid*, but to a less extent than free benzoic acid. By hydrolysis of the mixture of benzoresinol and resinotannol cinnamates the two alcohols are obtained, *benzoresinol* $C_{16}H_{26}O_2$, consisting of white crystals, and *resinotannol* $C_{18}H_{20}O_4$, a brown amorphous powder.

Siamese benzoïn also examined by Lüdy (Arch. Pharm. 231, 461) differs from Sumatra benzoïn by containing no cinnamic acid either free or combined, the main constituent being a mixture of a little benzoresinol benzoate with much *siaresinotannol benzoate*. The total amount of benzoic acid from both esters was 38·2 p.c. The alcohols obtained by the hydrolysis of the resin are present in the proportion of about 1 : 11. The benzoresinol is identical with that obtained from Sumatra benzoïn and crystallises in white prisms; m.p. 272°. *Siaresinotannol* $C_{12}H_{14}O_3$ is a brown powder very similar to resinotannol obtained from benzoïn of Sumatra. To distinguish between Sumatra and Siam benzoïn, 0·5 grm. is slowly heated to 40° C. with 10 c.c. potassium permanganate solution, when the Sumatra variety gives the odour of benzaldehyde (U.S.P.).

Benzoïn, with the exception of woody fragments always present in the cake variety, should dissolve in five times its weight of alcohol, and this solution should give with water a milky emulsion having an acid reaction; not less than 75 p.c. of Sumatra and 90 p.c. of Siam benzoïn should be soluble in alcohol. Adulteration with resin may be detected by warming with petroleum benzine or carbon disulphide, washing the benzin solution with sodium bicarbonate and then with water, and finally shaking with copper acetate solution: a green colour indicates the presence of resin.

Peru. *Balsamum Peruvianum*, B.P.; U.S.P. (*Baume de Pérou*, Fr.; *Perubalsam*, Ger.)

A dark molasses-like liquid obtained in the State of Salvador in Central America from trees of *Myroxylon Pereiræ* (Klotzsch). Description, *v.* Bentl. a. Trim. 83. Balsam of Peru was probably introduced into Europe soon after the Spanish conquest of Guatemala in 1524 (Flück. a. Hanb. 206). The bark is bruised and scorched late in the autumn, and the exudation excited by this means is collected (Flück. a. Hanb. 207; Dorat, Amer. J. Pharm. [3] 8, 302; Hanbury, Pharm. J. [3] 5, 241, 315).

Balsam of Peru sinks in water, in which it is insoluble. It has a sp.gr. of 1·140 to 1·158 (1·130–1·160 at 25°, U.S.P.). It is soluble in absolute alcohol, chloroform, acetone, and glacial acetic acid. Examined by Kraut (Annalen, 152, 129) and Kachler (Ber. 2, 512), the chief constituent of Peru balsam was supposed to be *cinnameïn*, benzyl cinnamate

$$C_6H_5{\cdot}CH:CH{\cdot}COOC_7H_7$$

Kachler's analysis of Peru balsam is:—cinnamic acid 46 p.c., benzyl alcohol 20 p.c., resin 32 p.c. *Cf.* Attfield (J. 1863, 557); Delafontaine (Z. 1869, 156) finds in addition to benzyl cinnamate, *cinnamyl cinnamate* or *styracin*. Trog. (Arch. Pharm. 232, 70) by suitable treatment has divided Peru balsam into two constituents, an oil and a resin. The liquid portion, known as cinnameïn to the earlier investigators, consists of benzyl benzoate with a small quantity of benzyl cinnamate and forms from 56 to 60 p.c. of the balsam; cinnamic acid and vanillin are present in very small proportions. The resin when hydrolysed yields cinnamic acid and a small proportion of benzoic acid and *peruresinotannol*, a resin alcohol of the formula $C_{18}H_{20}O_5$. The balsam has also been examined by Thoms (Arch. Pharm. 237, 271).

The B.P. demands that at least 57 p.c. shall remain in ethereal solution after shaking with *N*/2 NaOH solution; this portion, termed cinnameïn, must have a saponification value of not less than 235. The U.S.P. requires an acid number 56 to 84 and 50 to 56 p.c. of cinnameïn, extracted by ether from 4·5 p.c. NaOH solution; the saponification value of the cinnameïn must be 235-238.

A useful test is that 1 grm. balsam should give a clear solution with 3 grms. chloral hydrate in 2 c.c. water. Among the adulterants used have been copaiba, gurjun colophony, Canada turpentine, storax, tolu alcohol, &c. The presence of turpentine may be detected by warming 1 grm. balsam with 5 c.c. purified petroleum benzine on a water-bath; the petroleum extract on evaporation should yield no smell of turpentine and give neither green nor blue colouration with a drop of nitric acid, showing absence of resin (U.S.P.). On shaking the balsam with water, a diminution in its volume will occur if alcohol has been added; the specific gravity also gives information as to the probable presence of alcohol.

(For other modes of testing, *v.* Hirschsohn (Pharm. Zeit. 16, 81); Flückiger (Pharm. J. [3] 12, 45); Schlickum (Arch. Pharm. [3] 20, 498); MacEwan (Pharm. J. [3] 15, 236); Andrée (Arch. Pharm. [3] 22, 561); Denner (J. Pharm. Chim. [5] 18, 259). Testing of balsams, resins, and gum-resins: Pharm. J. [3] 17, 547.)

A *White Peru Balsam* is sometimes prepared in Salvador by expression from the fruit of the *Myroxylon Pereiræ*. It is a golden yellow semi-fluid granular crystalline mass containing a crystalline resin, *myroxocarpin* $C_{24}H_{34}O_3$, together with *styrolene*, *styracin*, and *cinnamic acid* (Stenhouse, Annalen, 77, 306; Pereira, Annalen, 77, 309; Scharling, Annalen, 97, 70; Harrison a. Malsch, J. 1875, 856). (For more recent investigations, *see* Germann (Arch. Pharm. 234, 641); Biltz (Chem. Zeit. 26, 436); Thoms a. Biltz (Chem. Zentr. 1904, ii. 1047); Hellström (Arch. Pharm. 243, 218). For other varieties of Peru balsam, *v.* Flück. a. Hanb. 210.)

Storax, *Liquid Storax*; *Balsamum Styracis*; *Styrax praeparatus,* B.P.; *Styrax,* U.S.P. (*Styrax Liquide,* Fr.; *Flüssiger Storax,* Ger.)

Storax balsam is derived from trees of *Liquidambar orientalis* (Miller), which are natives of Asia Minor (*cf.* Bentl. a. Trim. 107). This liquid storax is nearly related to another harder resin—the exudation of the *Styrax officinale* (Linn.). Both have been known since the later Greek period, but the latter is now no longer an article of commerce. Storax has been identified in the resins obtained from embalmed Egyptian mummies dating back about 3000 years (Tschirch and Reuter, Arch. Pharm. 250, 170). To obtain the storax the outer bark of the tree is removed, and the inner bark is collected and boiled in water. The balsam melts and rises to the surface and is skimmed off.

Liquid storax is heavier than water, about the consistence of honey, and of a greyish-brown colour. It always contains a little water, which imparts to it a greyish opacity. When this is removed, by long standing or by heat, the resin becomes quite transparent. Dried in this way it is soluble in alcohol, ether, carbon disulphide, and volatile oils; but not in light petroleum. The odour of storax is agreeably balsamic and the taste aromatic and pungent. Examined with a microscope crystals may be detected which have been identified, the feathery spicular crystals as styracin, and the rectangular tables and short prisms as cinnamic acid.

Storax contains 10 p.c. to 20 p.c. of water, 13 p.c. to 18 p.c. of woody and inorganic impurities, leaving 56 p.c. to 71 p.c. of matter soluble in alcohol, which consists chiefly of styrene, metastyrene, cinnamic acid, styracin, and a large proportion of resin (Flück. a. Hanb. 275). The alcohol-soluble part constitutes the *styrax praeparatus* of the B.P.

Styrene or phenylethylene $C_6H_5 \cdot CH : CH_2$ is obtained as a colourless mobile liquid by distilling storax with water (Bonastre, J. Pharm. Chim. 16, 88; Simon, Annalen, 31, 267). The solid polymeride of styrene, *metastyrene,* is also said to exist in storax. *Cinnamic acid* to the extent of 6 p.c. to 12 p.c. is obtained by boiling the balsam with sodium carbonate solution, which extracts it as a sodium salt from which the free acid is liberated by mineral acids.

Styracin or *cinnamyl cinnamate*

$$C_6H_5 \cdot CH : CH \cdot COOC_9H_9$$

was originally discovered in storax by Bonastre. It may be obtained, after removal of the styrene and cinnamic acid by treatment of the residue with ether, alcohol, or light petroleum in the form of a liquid, which with difficulty assumes a solid crystalline form, the crystals melting at 44° (Simon, Annalen, 31, 273; Toel, Annalen, 70, 1; Miller, Annalen, 188, 200). Styracin is readily converted by alkali into cinnamyl alcohol and cinnamate. *Benzyl alcohol* has been detected as a constituent of storax by Laubenheimer (Annalen, 164, 289). A good bibliography will be found in W. von Miller's memoir on the Chemical Compounds contained in Liquid Storax (Annalen, 188, 184), in which the author describes as present, in addition to the constituents already mentioned, *phenylpropyl cinnamate*, *ethyl cinnamate*, *ethyl vanillin*, large quantities of two alcoholic compounds, *α*- and *β-storesin*, and their cinnamic esters, a *sodium compound of storesin* and a *resin*. Dieterich showed that Miller's ethyl vanillin was really vanillin (Pharm. Centralhalle, 1896, No. 28). According to v. Itallie (Chem. Zentr. 1901, ii. 856), a good specimen of storax contains about 2·4 p.c. of substances insoluble in ether, 23·1 p.c. of free cinnamic acid, 14 p.c. of water, 22·5 p.c. of aromatic esters, 2 p.c. of styrene and vanillin, and 36 p.c. of resin. The total proportion of cinnamic acid is about 43 p.c.; the combined acid occurring partly in the resin and partly in the aromatic esters.

The B.P. demands an acid value between 60 and 90, and an ester value between 100 and 146; the U.S.P. an acid value of 56–85 and a saponification value of 170–230. Storax is sometimes adulterated with turpentine. To detect this Hager dissolves the balsam in a little warm alcohol, and shakes this solution with light petroleum. The light petroleum on evaporation leaves a residue in which the terebinthinous odour is concentrated, and may be readily detected. Further, the residue so obtained, in the case of genuine storax, is colourless with a bluish opalescence, and represents 45–55 p.c. of the original balsam; but if turpentine be present the percentage is larger, and the residue has a yellowish colour (Ph. Centh. 15, 163).

Closely allied to liquid storax are the exudations from the *Styrax officinale* (Linn.), *Liquidambar styraciflua* (Linn.), a native of North America, the balsam of which was examined by Flückiger and v. Miller (Arch. Pharm. [3] 20, 646, a. 648). It is obtained in the form of a sticky grey mass containing white crystalline portions mixed with fragments of wood and bark. Its composition does not differ essentially from that of Asiatic Storax (*v.* Itallie). *Liquidambar formosana* (Hance); and *Altingia excelsa* (Noronha) (*cf.* Flück. a. Hanb. 276; Tschirch a. v. Itallie, Arch. Pharm. 239, 541).

Tolu. *Balsamum tolutanum,* B.P.; U.S.P. (*Baume de tolu,* Fr.; *Tolubalsam,* Ger.)

Monardes, in his book published in 1574, describing the products of the West Indies, is the first to mention balsam of tolu. Soon afterwards it was introduced into England. Tolu is the product of the trees of *Myroxylon toluiferum* (H. B. a. K.), natives of Venezuela and New Granada, and probably also of Ecuador and Brazil. Considerable amounts are exported by Bolivia. (For botanical characters, *v.* Bentl. a. Trim. 84.) V-shaped incisions are made, and the concreted juice from time to time collected. This draining of the trees goes on for eight months of the year (Weir, Journ. R. Hort. Soc., May, 1864).

Balsam of tolu is a viscid resin or plastic solid, which on exposure hardens and is brittle in cold weather. It has an agreeable odour suggestive of vanilla, and has a decided aromatic taste. Crystals of cinnamic acid may be seen in tolu when thin layers are examined. It is soluble in alcohol (1 in 1), glacial acetic acid (1 in 1), chloroform (2 in 1), benzene (1 in 3), acetone, also in caustic potash. Carbon disulphide dissolves it partially, removing chiefly cinnamic acid. Balsam of tolu consists for the most part of an *amorphous resin* similar to that left by carbon disulphide in the case of Peru balsam. This resin on hydrolysis yields *tolu-resinotannol* $C_{17}H_{18}O_5$, a lower homologue of peruresinotannol, a dark brown powder decomposing at 100° without melting. It gives colour reactions with ferric chloride and potassium dichromate, and precipitates with lead acetate and gelatin (Oberländer, Arch. Pharm. 232, 559). Treatment with water extracts from balsam of tolu *cinnamic acid* (Carles, J. Pharm. Chim. 19, 112), and according to Busse (Ber. 9, 830) it contains also *benzoic acid*, and both *benzyl benzoate* and *cinnamate*. Distilled with water, small quantities of a peculiar hydrocarbon pass over which has been called *tolene*. The yield, according to Deville, is 2 p.c. (Ann. Chim. Phys. [3] 3, 152). Tolene has the formula $C_{10}H_{16}$. Its sp.gr. at 10° is 0·858 (Kopp), and it boils at 170°, according to Deville and Scharling, or at 154°–160° (Kopp). Deville found tolene to have a vapour density of 5·1. This hydrocarbon does not appear to have been further studied or to be known in any other chemical relation.

Colophony present as an adulteration in tolu may be detected by extracting 1 grm. with 25 c.c. of carbon disulphide and filtering; on evaporation the residue, dissolved in glacial acetic acid, does not become green on adding a few drops of sulphuric acid. The carbon disulphide, or light petroleum extract, filtered and shaken with 0·1 p.c. copper acetate, does not become green (Hirschsohn, Chem. Zentr. 1895, ii. 694). Added colophony is also detected by the saponification number of the residue left on evaporation of the carbon disulphide. If the residue falls below 25 p.c. the addition of exhausted balsam may be suspected. When turpentine has been added, sulphuric acid produces a black instead of the normal cherry-red colour. The U.S.P. demands saponification value 154–220 and acid value 112–168 for tolu balsam; the B.P. requires 107·4–147·2 for acid value, and a saponification number of 107–202.

Xanthorrhœa Balsams. A number of balsamic resins are obtained from the xanthorrhœas or grass trees of Australia. Seven species of these, the *arborea*, *australis*, *Hastile*, *media*, *minor*, *bracteata*, and *Pumilio* were described as early as 1810 by Brown (Prodromus Novæ Hollandiæ). The first two are arborescent trees, the third and fourth have short stems, and the last three are stemless. Hirschsohn (Pharm. Zeit. 16, 81) distinguishes three xanthorrhœa balsamic exudates; but of these only two are important, the *yellow* or *acaroid balsam* and the *red balsam* (Pereira, Mat. Med. 3rd ed. 1099).

Acaroid Balsam, *Acaroid Resin*, *Resina Acaroides*, *Resin of Botany Bay*. This balsam was first mentioned by Governor Phillips in 1789 (Voyage to Botany Bay). It exudes spontaneously from the *Xanthorrhœa Hastile* and, according to some writers, from the *X. arborea*. It has a yellow colour resembling gamboge, and when heated evolves a balsamic odour. It is used in the preparation of sealing-wax and lacquers and japanner's gold-size. Rudling found for the yellow resin an acid value of 65–90, a saponification value of 100–150, and an iodine value of 175–176 (Chem. Rev. Fett. v. Harz. Ind. 1903, 10, 51). It may be identified by heating with nitric acid, dissolving the cold residue in alcohol and adding 10 drops of 5 p.c. ferric chloride solution. A brownish-black colour and turbid appearance denotes the presence of acaroid resin (Rebs, Lack. und. Farb. Ind. 1908, No. 11). Its chief constituents are *resin*, a trace of *volatile oil*, and *cinnamic*, *benzoic*, and *para-coumaric acids*, also *para-hydroxybenzaldehyde* and probably vanillin (Bamberger, Monatsh. 14, 333). The resin consists of *xanthoresinotannol* $C_{43}H_{46}O_{10}$, chiefly in form of *para-coumarate* (Hildebrand, Arch. Pharm. 234, 698). (For properties of xanthorrhœa resin oil, *see* Schimmel and Co. (Chem. Zentr. 1898, i. 258); Haensel (Chem. Zeit, 1908, i. 1837).) By distilling acaroid balsam, Stenhouse obtained a light neutral oil containing *benzene* and *cinnamene*, and by treatment with nitric acid the same observer finds acaroid balsam to give so large a yield of *picric acid* that he recommends it as a convenient source of that compound. As much as 13 p.c. of *parahydroxybenzoic acid* is formed when acaroid balsam is fused with potash. Amongst the other products of this reaction, are *resorcinol*, *pyrocatechol*, and a *double compound of para-hydroxybenzoic and protocatechuic acids* $C_{14}H_{12}O_7,2H_2O$, which has been likewise obtained from benzoin (Hlasiwetz and Barth, J. 1866, 630).

Red Acaroid Balsam. Grass-tree Gum. Black-boy Gum. A red balsamic resin resembling dragon's blood, and obtained chiefly from *Xanthorrhœa australis*. When heated it evolves a balsamic odour. This resin does not contain cinnamic or benzoic acid, it contains a small quantity of *para-hydroxybenzaldehyde*, and consists mainly of *erythroresinotannol* $C_{40}H_{40}O_{10}$, chiefly as *para*-coumarate (Bamberger, Hildebrand). Its solution in alcohol stains a deep mahogany colour. A red acaroid balsam is also obtained from the Bahamas, which is lighter in colour than the Australian variety. It is similar in composition to the latter, except that it contains cinnamic acid. Grass-tree resins are used in the preparation of spirit lacquers, varnishes, sealing-wax, &c. During the European War considerable quantities of picric acid were made from the different varieties of *xanthorrhœa* resins.

BAMBARA FAT *v.* Bassia oils.

BAMBOO. The ash of the shoots of these grasses (*Bambusa arundinacea* (Willd), *Gigantochloa verticillata* (Munro), &c.) contains from 30 to 40 p.c. of potash (K_2O), and constitutes a good source of potash. The fibres of the shoots supply an excellent paper-making material, and have been used for this purpose by the Chinese from time immemorial (Romanis, Chem. News, 45, 158; 46, 51; Nature, 18, 50).

BAMBOOI FAT or **BAMBUK BUTTER** *v.* Bassia oils.

BANANA. The fruit of *Musa sapientium*, a plant growing freely in tropical countries. When ripe the pulp is rich in sucrose and invert sugar, but in the unripe condition contains much starch, and is extensively used for the preparation of banana flour in the Indian Archipelago, Brazil, the west coast of Africa, and the Pacific Islands.

Analyses by Leuscher (Zeitsch. öffentl. Chem. 1902, 8, 125) of (1) green husks, (2) ripe husks, (3) unripe fruit (pulp), (4) ripe fruit (pulp), and (5) banana-meal, are as follows:—

	(1)	(2)	(3)	(4)	(5)
Water . .	70·0	70·0	70·5	67·1	15·0
Crude protein .	2·0	2·9	3·9	5·0	7·0
Crude fat .	4·5	4·1	0·1	0·2	0·3
Crude fibre .	9·9	8·6	0·4	0·3	5·9[1]
N-free extract .	8·3	10·4	—	—	70·0
Starch . .	—	—	19·1	—	
Dextrin . .	—	—	2·6	1·0	
Tannin . .	—	—	2·2	0·1	
Sucrose . .	—	—	—	15·8	
Invert sugar .	—	—	—	9·7	
Ash . .	5·3	3·9	1·1	0·9	1·8

Only the quite green fruit, containing mere traces of sugar, can be used for preparing the meal.

• Ripe bananas contain *invertase* (Mirran, Chem. Zeit. 1894, 17, 1283). American analyses show much less protein in ripe bananas than is given in Leuscher's figures, the average being only 1·3 p.c. (Bulletin 28, U.S. Dept. of Agriculture, 1899).

The pulp appears to contain small quantities of amyl acetate, to which its characteristic aroma is due.

For a study of the relative amounts of sucrose, invert sugar and starch present in the fruit dried at temperatures between 40° and 105°, *see* Waterman (Chem. Weekblad, 1915, 12, 552). For a study of the changes in composition of ripening bananas, *see* Gore (J. Agric. Research, 1914, 3, 187).

The stalks and skins of bananas are rich in potash, and have been suggested as worth collecting for manurial purposes (Ellis, Jour. Soc. Chem. Ind. 1916, 456 and 521). The following figures were quoted:—

	Stalks.	Skins.
Moisture . . .	91·6 p.c.	88·2 p.c.
Dry matter . .	8·4 „	11·8 „
Ash, in original .	2·4 „	1·8 „
Potash, in original .	1·1 „	1·0 „
Ash, in dry matter .	29·9 „	15·0 „
Potash, in dry matter .	13·7 „	9·0 „
Potash in ash . .	45·9 „	57·2 „

It is estimated that the bananas imported into this country per annum (about 9,000,000 bunches) include, on the average, about 16,000 tons of stalks and 60,000 tons of skins, containing about 160 tons and 600 tons of potash, respectively.

BANDROWSKI'S BASE. Tetra-amino-diphenyl-*p*-azophenylene.

BAPTISIN *v.* GLUCOSIDES.

BAPTITOXINE *v.* CYTISINE.

BARBALOIN *v.* GLUCOSIDES.

BARBATIC ACID. *Barbatic acid* $C_{19}H_{20}O_7$ was first isolated from the lichen *Usnea barbata* by Stenhouse and Groves (Chem. Soc. Trans. 1880, 37, 405), in which it occurs in conjunction with usnic acid. Zopf (Annalen, 1897, 297, 271) found barbatic acid in the *Usnea longissima*, in the *Electora ochrole uca* (*ibid.* 1899, 306, 282), and in the *Usnea dasypoga* (*ibid.* 1902, 324, 39); Hesse (J. pr. Chem. 1898, ii. 57, 232) describes its presence in the *Usnea longissima*, *Usnea barbata*, and *Usnea ceratina*. Hesse (*l.c.* originally considered that barbatic acid had the composition $C_{22}H_{24}O_8$, and described potassium barium and copper salts and an ethyl ester, m.p. 132°, which apparently established this formula, but in a later paper (J. pr. Chem. 1903. ii. 68, 1) he adopted Stenhouse and Groves' formula, $C_{19}H_{20}O_7$. The *sodium salt*

$$C_{19}H_{19}O_7Na, 2H_2O$$

crystallises in straight-sided leaflets (*cf.* also Zopf, 1902, 789). The action of acetic anhydride on barbatic acid leads to the formation of a compound which is probably the lactone of acetylbarbatic acid; this melts at 250° and on recrystallisation from acetic anhydride yields *acetylbarbatic acid* $C_{19}H_{19}(C_2H_3O)O_7$, m.p. 172°. By the hydrolysis of barbatic acid with aqueous alkalis *betorcinol* and *rhizoninic acid* are formed. Barbatic acid crystallises in colourless needles, m.p. 184° (Hesse, J. pr. Chem., 1906 (2), 73, 113). A. G. P.

BARBERRY. Barberry or berberry, *Berberis vulgaris*, is a compact bush which attains to a height of from 8 to 10 feet, and is found wild in Great Britain and throughout most parts of Europe and North America. The colouring matter present is *berberine*, and this, though occurring mainly in the bark, is also present in the stem and root of the plant.

Until recently a concentrated commercial extract of this material, known as 'Barberry extract,' was to be found on the market, and employed for dyeing silk and leather. It does not appear to have been at any time extensively used for these purposes, and is now apparently obsolete.

Barberry is, however, interesting, in that it contains the only natural basic dyestuff at present known, and may, in fact, be applied to fabrics in the same way as the artificial basic colouring matters. Silk and wool, for instance, may be dyed yellow by means of a faintly acidulated decoction of the material, preferably at from 50° to 60°, whereas for cotton, a tannin antimony mordant is necessary.

For the isolation of berberine the procedure is simple, and consists merely in extracting the ground dyestuff with boiling water containing a slight excess of lead acetate. The concentrated extract is mixed with hydrochloric acid when, on cooling, crystals of berberine hydrochloride separate. Berberine hydrochloride, $C_{20}H_{18}O_4NCl$,[1] when pure, crystallises in long silky needles which possess an intense yellow colour and are soluble in hot water and alcohol. The most reliable of the earlier analyses of berberine are those given by Perrins (Annalen, Supp. 2, 176), who suggested the formula $C_{20}H_{17}NO_4$, but it is now known that berberine has the composition $C_{20}H_{19}NO_5$. The base

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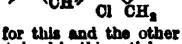
[1] Including tannin and colouring matter.

[1] The substance commonly known as *berberine hydrochloride* is, in fact, not a hydrochloride, but a quaternary chloride containing the grouping given below, and should be named *berberinium chloride* (W. H. Perkin, Chem. Soc. Trans. 1918, 113 503)—



The old names for this and the other salts described are, however, retained in this article.

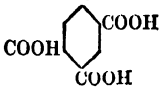
berberine (or berberinal) is best obtained by adding strong caustic soda to the aqueous solution of the sulphate and extracting the product with ether, from which it separates in yellow needles and melts at 144° (Gadamer, Archiv. der Pharm. 1905, 243, 34). Berberine is a strong base, yielding well-defined crystalline salts of a deep yellow colour, of which the following may be given as examples:—

Berberine nitrate $C_{20}H_{18}NO_4{\cdot}NO_3$, *Berberine hydrochloride*, $C_{20}H_{18}NO_4Cl$, *Berberine hydriodide* $C_{20}H_{18}NO_4I$, and *Berberine platinichloride* $(C_{20}H_{18}NO_4)_2PtCl_6$.

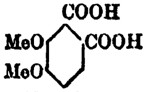
The most important of the early work on berberine is that of Hlasiwetz and Gilm (Jahres. 1864, 407), who by reducing the base with zinc and sulphuric acid prepared *tetrahydroberberine* $C_{20}H_{21}NO_4$, and by fusion with alkali obtained the acids $C_9H_8O_5$ and $C_8H_8O_5$, the second of which was termed *berberinic acid*. Perkin (Chem. Soc. Trans. 1889, 55, 89), who subsequently examined this latter compound and found that its properties agreed in all respects with those given by Hlasiwetz and Gilm, has shown that it possesses the constitution of a *homocatechol carboxylic acid*.

Interesting also is the fact that by the alkali fusion of berberine, or by distilling it with lime, Bernheimer and Bödecker isolated an oily base which they regarded as quinoline, but which is now known to be *iso-quinoline*.

The most valuable results, however, have been afforded by a study of the oxidation products of berberine hydrochloride. Weidel, who employed nitric acid for this purpose, obtained *berberonic acid*, $C_8H_5NO_6$, which he rightly regarded as a pyridine tricarboxylic acid, and this has been more recently shown to consist of the 2 : 4 : 5 compound—



whereas Schmid and Schilbach (Arch. Pharm. [3], 25, 164) by the action of permanganate obtained some quantity of *hemipinic acid*—



Subsequently, W. H. Perkin, junr. (Chem. Soc. Trans. 1889, 55, 75; 1890, 57, 991; 1910, 97, 323) published a series of elaborate researches on this subject, and it is almost entirely to these that our present knowledge of berberine is due. By adopting special precautions and by the employment of a very large quantity of material, this author succeeded in obtaining from berberine hydrochloride by the action of permanganate, numerous important compounds, the study of which gave the clue to its constitution. The operations employed are of too involved a nature to be dealt with in detail here, but a general idea of the methods employed can be gathered from the scheme given below, drawn up by the investigator himself (*l.c.* 1890).

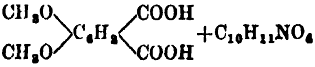
Among the oxidation products of berberine, anhydroberberilic acid and berberal have proved to be the most important, and these only will be discussed here in detail.

Anhydroberberilic acid $C_{20}H_{17}NO_8$, as its name denotes, is an anhydro derivative of berberilic acid, into the sodium salt of which it is readily transformed by the gentle action of sodium hydroxide solution—

$$C_{20}H_{17}NO_8+2NaOH=C_{20}H_{17}NO_9Na_2+H_2O$$

Berberilic acid, $C_{20}H_{19}NO_9$, though only slowly attacked by alkalis, is readily hydrolysed by boiling dilute sulphuric acid, and Perkin thus obtained hemipinic acid and a basic compound $C_{10}H_{11}NO_4$—

$C_{20}H_{19}NO_9+H_2O=$

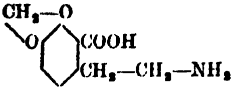


$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!\!>\!C_6H_2\!<\!\!\begin{matrix}COOH\\COOH\end{matrix}+C_{10}H_{11}NO_4$$

This latter substance proved to consist of *a-aminoethylpiperonyl-carboxylic acid*—

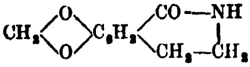
BERBERINE HYDROCHLORIDE IS OXIDIZED WITH POTASSIUM PERMANGANATE, THE PRODUCT TREATED WITH SULPHUROUS ANHYDRIDE AND FILTERED.

<table>
<tr><td colspan="4">*Yellow Precipitate* treated with Warm Dilute Sodium Carbonate Solution and filtered.</td><td colspan="6">*Yellow Filtrate* evaporated to Half its Bulk and filtered.</td></tr>
<tr><td colspan="3">*Residue* boiled with acetic acid and filtered hot.</td><td rowspan="5">*Solution* contains berberilic acid, $C_{20}H_{19}NO_9$ and some anhydroberberilic acid, $C_{20}H_{17}NO_8$</td><td rowspan="5">*Precipitate* contains oxyberberine, $C_{20}H_{17}NO_5$, dioxyberberine, $C_{20}H_{17}NO_6$, anhydroberberilic acid, $C_{20}H_{17}NO_8$</td><td colspan="5">*Solution* evaporated to half its bulk and extracted twenty times with ether.</td></tr>
<tr><td rowspan="4">*Residue* contains berberine hydrogen sulphite, $C_{20}H_{17}NO_4$, H_2SO_3</td><td colspan="2" rowspan="2">*Solution* on cooling deposits crystals which are separated by filtration.</td><td colspan="4">*Ethereal solution* evaporated, residue boiled with dilute sodium carbonate solution and filtered hot.</td><td rowspan="4">*Aqueous solution* contains hemipinic acid, $C_{10}H_{10}O_6$, ω-amidoethylpiperonylcarboxylic anhydride, $C_{10}H_9NO_3$, and inorganic salts.</td></tr>
<tr><td rowspan="3">*Residue* contains hemipinic anhydride, $C_{10}H_8O_5$</td><td colspan="3">*Solution* allowed to cool and filter.</td></tr>
<tr><td rowspan="2">*Residue* consists of anhydroberberilic acid, $C_{20}H_{17}NO_8$</td><td rowspan="2">*Solution* contains berberal, $C_{20}H_{17}NO_7$</td><td rowspan="2">*Crystals* of ω-amido ethylpiperonylcarboxylic anhydride, $C_{10}H_9NO_4$</td><td colspan="2">*Solution* acidified with hydrochloric acid and filtered.</td></tr>
<tr><td>*Residue* contains berilic acid, $C_{20}H_{18}NO_8$</td><td>*Solution* contains hydrastic acid, $C_9H_6O_6$, and hemipinic acid, $C_{10}H_{10}O_6$</td></tr>
</table>

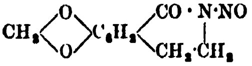


and the main facts which lead to the determination of its constitution are as follows :—

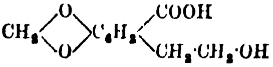
When boiled with water, it readily loses the elements of water with production of the anhydride—



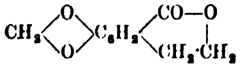
which reacts with nitrous acid to give the nitroso derivative—



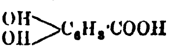
and this compound with dilute caustic soda evolves nitrogen with the production of *ω-hydroxyethylpiperonyl-carboxylic acid*—



The anhydride—

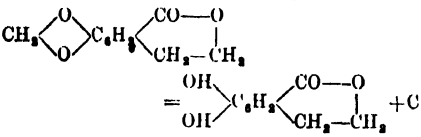


readily obtained from this latter by merely boiling with water, when fused with alkali yields *catechol* and *protocatechuic acid*—



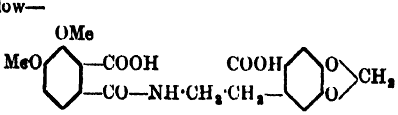
$$\begin{matrix}OH\\OH\end{matrix}\!>C_6H_3{\cdot}COOH$$

and by the action of hydrochloric acid at 170°–175° is converted with loss of carbon, a reaction characteristic of piperonal derivatives, into *hydroxyethylcatechol-carboxylic anhydride*—

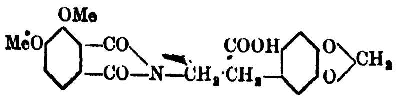


As the result of these experiments, there could be little doubt that berberilic acid (1) and its anhydride (2) possess the constitutions given below—

(1)

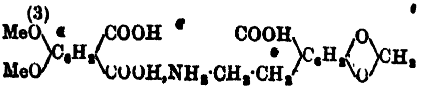


(2)



and that these are correct was subsequently established by the observation that the hemipinate of ω-aminoethylpiperonyl-carboxylic acid (3) on heating is transformed into anhydroberberilic acid—

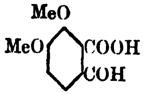
(3)



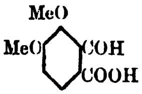
Berberal. As in the case of berberilic acid, the constitution of berberal has been established mainly by a study of the products of its hydrolysis. By the action of alcoholic potash it yields ω-aminoethylpiperonyl-carboxylic acid and an acid $C_{10}H_{10}O_5$, and thus resembles berberilic acid which under similar conditions gives hemipinic acid in the place of this latter.

The acid $C_{10}H_{10}O_5$ on examination proved to be constituted similarly to opianic acid (1), and was, therefore, termed *pseudo-opianic acid* (2)—

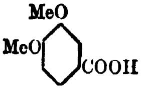
(1)



(2)

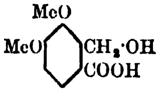


Thus by the action of caustic potash solution it gave veratric acid—

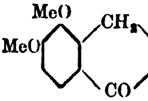


and when reduced formed the unstable acid (3) which readily passed into *pseudomeconine*—

(3)



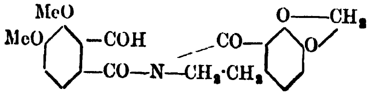
(4)



Perkin now found that whereas pseudo-opianic acid and ω-aminoethylpiperonyl-carboxylic acid on heating together give first the salt of the base, that this subsequently by elimination of water passes into berberal—

$$C_{10}H_{10}O_5 + C_{10}H_9NO_3 = C_{20}H_{17}NO_7 + H_2O$$

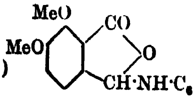
Apparently, therefore, berberal could be represented as follows :—



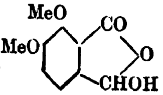
and this formula was at first adopted.

Liebermann, however (Ber. 1896, 29, 175), subsequently pointed out that when opianic acid reacts with aniline to form anilinoopianic acid (1) the latter behaves as a derivative of hydroxyphthalide (2)—

(1)

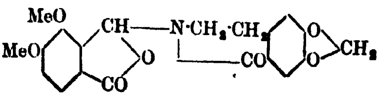


(2)

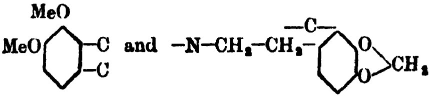


and it is now generally accepted that in the condensations of opianic acid with basic substances, it is always the carbon atom of the aldehyde group which becomes attached to the nitrogen in the final product.

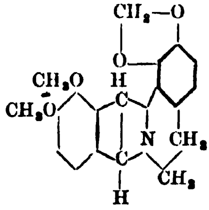
As a result of this later work, Perkin and Robinson have modified the original expression for berberal as follows :—



An examination of the formulæ both of berberilic acid and of berberal, led Perkin in 1890 to the consideration that in berberine the following groups of atoms are present—



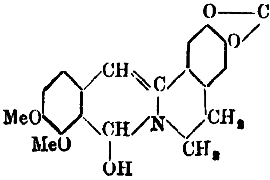
and that, in order to construct a formula for this alkaloid, these require to be united with the addition of but one atom of hydrogen. As a result the following constitution was assigned to this alkaloid—



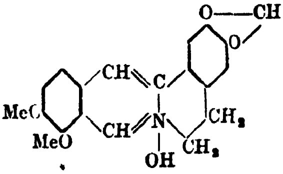
this structure being based upon the older formula of berberine, $C_{20}H_{17}NO_4$, which at that time was considered to be correct.

Subsequently Perkin and Robinson pointed out that the methylenedioxy-group in Perkin's original formula had been incorrectly placed, as was evident from an examination of the structure of ω-aminoethylpiperonyl-carboxylic acid (*cf.* also Freund and Beck, Ber. 1904, 37, 4673). Moreover, as a result of the newer views of the former authors as to the constitution of berberal (*l.c.*) the position of the methoxy groups in the old berberine formula required modification. It is now considered that berberine has the formula $C_{20}H_{19}O_5N$, and is represented by formula (1), and that for the purpose of salt formation it undergoes change into the modification called berberinium hydroxide (2), from which the salts are obtained by the replacement of the OH group by the acid radical—

(1)

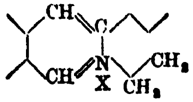


(2)



The reasons for this assumption (W. H. Perkin, jun., Chem. Soc. Trans. 1918, 113, 503) are based on the similarity between berberine and cotarnine, but are too complex to enter into in this article, and for their understanding the literature must be consulted (*cf.* Robinson and Robinson, Trans. 1917, 111, 958).

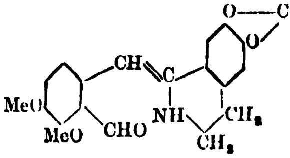
Interesting is the fact that though the salts of berberine are derived from the hydroxyl formula and contain the grouping—



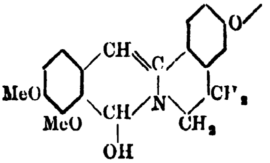
(where X=Cl, HSO_4, NO_3, &c.), the alkaloid itself exists as a different modification.

When berberine sulphate is treated with barium hydroxide (Gadamer), a strongly alkaline liquid is produced which possibly contains the hydroxy modification of berberine (berberinium hydroxide), but if to this solution excess of sodium hydroxide is added, the yellow modification known as *berberinal* is obtained. The constitution assigned to this substance by Gadamer was—

(1)



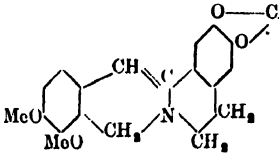
but its most probable structure is that represented by the formula—



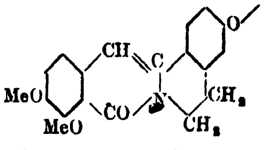
(*cp.* Tinkler, Chem. Soc. Trans. 1911, 99, 1345).

When treated with excess of alkali, berberinal yields dihydroberberine (1) with simultaneous formation of oxyberberine (2), owing, according to Gadamer, to the conversion of the COH group into $CH_2(OH)$ and COOH in the manner characteristic of aromatic aldehydes—

(1)



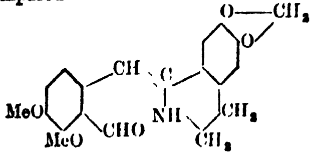
(2)



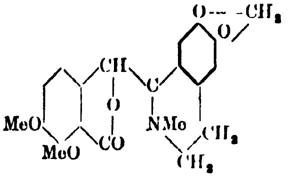
The latter compound was first obtained by Perkin as an oxidation product of berberine.

On the other hand, Faltis (Monatsh. 1910, 31, 557) considers the reaction of berberinal with alkali to be similar to that which takes place between quinoline methiodide under the same conditions and that the products of the reaction are oxyberberine and tetrahydroberberine (*cf.* Dekker, 1903, 1205 and 2568). It has, however, been shown conclusively that Faltis' view is incorrect (W. H. Perkin, private communication).

Berberine is closely allied to hydrastine, which occurs along with it in *hydrastis canadensis*, and the relationship between these compounds is clearly evident, if the formula of Gadamer for berberinal and that of hydrastine (*see* above) are compared—



Berberinal.



Hydrastine.

In 1911 Pictet and Gams (Ber. 1911, 44, 2480) were successful in effecting the synthesis of berberine by the following series of reactions. Homopiperonylamine,

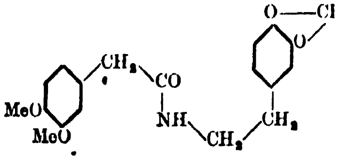
$$CH_2 : O_2 : C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$$

by condensation with the chloride of homo veratric acid,

$$(CH_3O)_2C_6H_3{\cdot}CH_2{\cdot}COCl,$$

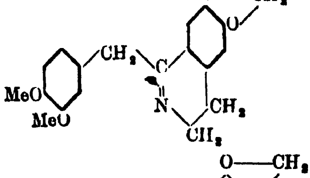
yields *homo-veratroyl-homopiperonylamine* (1) —

(1)

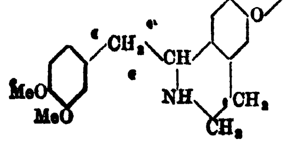


and this compound on treatment with phosphorus pentoxide in the presence of boiling xylene is transformed into the dihydro-quinoline base (2). By reduction with tin and hydrochloric acid this passes into *veratroyl-methylene-dioxy-tetrahydro-iso-quinoline* (*veratryl norhydrohydrastinine*) (3)—

(2)

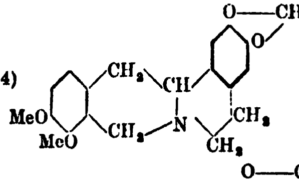


(3)

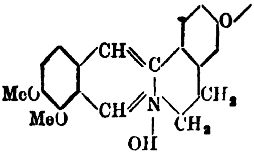


which on treatment with methylal, $CH_2(OCH_3)_2$, gives *tetrahydroberberine* (4), a compound originally prepared by Hlasiwetz and Gilm, and subsequently examined by Perkin and others. This by the action of mild oxidising agents such as iodine or mercuric acetate is readily transformed into berberine (5)—

(4)



(5)



For the synthesis of oxyberberine the paper of Pictet and Spengler (Ber. 1911, 44, 2036) must be consulted.

Numerous plants contain berberine, and though most of these have been or are used medicinally, their employment for dyeing has apparently been of rare occurrence. The following list embodies most of these :—

Berberis aquifolium (Gordin, Arch.. Pharm. 1902, 240, 146), *B. aetnensis* (Perkin, Chem. Soc. Trans. 1897, 71, 1198), *Cossinium fenestratum* and *Xanthorrisa aquifolia* (Perrins, Annalen, 83, 276), *Hydrastis canadensis* (Mahla, Amer. Chem. J. [2], 33, 843), *Coptis aceta* and *C. trifolia, Chelidonium majus* and *Stylophorum diphyllum* (Schlotterbeck, Amer. J. Pharm. 1902, 74, 584), *Evodia meliæfolia* and *Toddalia aculeata* (Perkin and Hummel, Chem. Soc. Trans. 67, 414), *Xanthoxylum clava Herculis* (Chevallier and Pelletan, Journ. de Chim. Médicale, 1826, 2, 314), yellow Assam wood or 'Woodumpar' (Crookes' Dyeing and Calico Printing), *Coelocline polycarpa* (Stenhouse, Annalen, 66, 384 ; 69, 40), *Archangelisa lemnis-cata* (Becc.) and *Mahonia nepalensis* (D.C.), (Brooks' Philippine Journ. of Science, 1910, v. 442).

For the commercial preparation of berberine the *Hydrastis canadensis*, which contains about 4 p.c. of the alkaloid, forms the best available material. A. G. P.

BARBITAL and **BARBITONE.** *See* VERONAL, PYRIMIDINES and SYNTHETIC DRUGS.

BARBITURIC ACID *v.* MALONYL CARBAMIDE.

BARILLA or **BARILLOR.** (Fr. *Barille.*) Commercial name of an impure soda obtained from the ashes of the *Salsola Soda* (Linn.), formerly grown specially in Spain, Sicily, Sardinia, the Canary Islands, and the Levant. The seed was sown at the end of the year, and the plants were ready for cutting in September of the following year ; they were usually burnt during October. A hole capable of holding one or two tons of soda was dug in the ground and covered over with an iron grating ; the dried plants, mixed with canes, were heaped on this and set on fire. The heat was sufficient to melt the ash, which ran down and collected in the hole. More

material was supplied to the fire till the hole was full of fused soda; it was then covered with earth and left to cool, after which the porous mass was broken out and was ready for shipment. Contained about 20 p.c. alkali, together with chlorides and sulphates of sodium, calcium and aluminium and very little sulphur. Formerly much used for making soda soap; little, if at all, used now.

Kelp is sometimes called British Barilla.

BARIUM. Symbol, Ba. At. wt. 137·37.

The name 'barote' (from βαρύς, heavy) was given to the earth contained in heavy-spar (*terra ponderosa*) by Guyton de Morveau in 1779, and was afterwards altered to 'baryta' by Lavoisier; the name itself, therefore, is indicative of the great density of its compounds. Barium occurs principally as the sulphate, *barytes* or *heavy-spar* $BaSO_4$, and is generally found associated with metallic ores containing sulphur. Dieulafait (Ann. Chim. Phys. [5] 15, 530) has shown that all primary rocks contain barium in sufficient quantity to be easily detected. Barium also occurs in nature as *witherite* $BaCO_3$, *barytocelestite* $(BaSrCa)SO_4$, *barytocalcite* $(BaCa)CO_3$, *alstonite* $(BaCa)CO_3$, and in certain varieties of the ores of manganese; also in certain silicates, as *brewsterite* $H_4(SrBa)Al_2Si_6O_{18},3H_2O$, *harmotome* $H_2(K_2Ba)Al_2Si_5O_{15}\cdot 4H_2O$, and *hyalophane* or *baryta-felspar* $K_2Ba\cdot 2Al_2Si_8O_{24}$, and frequently in mineral waters. Barium is also frequently found in calcium and strontium minerals, replacing a portion of those elements with which it is isomorphous.

It is never found native. Its oxide, baryta BaO, was first recognised as a peculiar earth distinct from lime by Scheele in 1774.

Preparation.—Davy (Phil. Trans. 1808, 354) electrolysed a moist paste of a barium salt, using a cathode of mercury. He thereby obtained a poor amalgam which on distillation yielded a silver-white solid that he believed to be metallic barium, but which in reality was only a rich amalgam as shown by Donath (Ber. 12, 745).

Bunsen (Pogg. Ann. 91, 619) slightly modified Davy's process, heating the amalgam in a charcoal boat in a current of hydrogen, obtaining a tumefied mass which was probably a mixture of hydride and carbide. Guntz has also shown that Kern's method (Chem. News, 31, 243) of heating the iodide with sodium yields a sub-iodide which decomposes water.

Clarke (Ann. Phil. 17, 419) exposed baryta to the action of the oxy-hydrogen blow-pipe flame on charcoal and obtained metallic-looking globules probably of barium carbide.

Matthiessen (Annalen, 93, 277) electrolysed the fused chloride and obtained metallic-looking globules which were probably sub-chloride.

Maquenne (Bull. Soc. chim. (3) 7, 368) heated the amalgam *in vacuo*, but owing to decrepitation of the substance and rupture of the tube he was unable to obtain satisfactory results.

Guntz (Bull. Soc. chim. [3] 29, 483), by studying the same process, was finally able to distil off all the mercury without decrepitation or bursting of the tube. After many experiments, he finally adopted the following method: An amalgam containing 3 p.c. of barium was prepared according to Davy's original process, and 5 to 6 kilos of it were distilled in an atmosphere of hydrogen under reduced pressure to such a point as to obtain an amalgam having a close grain and not readily oxidisable, containing about 10 p.c. barium. About half a kilo. of it was then placed in an iron boat contained in a large porcelain tube. Over the boat was placed a nickel spiral to prevent spurting and loss. The tube was then heated very slowly by an electric current circuit so as to arrive at a dull red heat in about four hours, a vacuum being maintained in the tube. The amalgam slowly loses mercury without change of form, and towards 900° it suddenly liquefies, when the current is turned off to avoid ebullition and loss. The amalgam so obtained, containing about 65 p.c. barium, has a coarsely faceted crystalline structure, and quickly oxidises in air. For the last operation it is placed in a nickel boat contained in a porcelain tube lined with nickel foil. The latter is necessary, as when the barium distils towards the end of the operation its corrosive action on the glass causes rupture. The tube is maintained at 900° for two or three hours under diminished pressure, keeping the ends of the tube suitably cooled; then at 950° for one hour during which time there is a considerable loss of barium. The barium so obtained is kept in an atmosphere of dry carbon dioxide. A sample obtained by distilling half the barium had the composition Ba 98·35, Hg 0·83, Fe 0·40. In repeated experiments Guntz failed to obtain barium much purer than 98 p.c. He, however, found in his later experiments that by preparation of the hydride a much purer metal could be obtained (Compt. rend. 141, 1240). The method is a modification of the earlier experiment. After the preparation of the metal in the above way pure dry hydrogen is allowed to enter the tube, maintained at 900°. It is then heated to 1200°, just below the fusion point of the hydride; by this means every trace of mercury can be removed. The hydride contained in a nickel boat is then placed in the nickel-lined tube, heated in a vacuum at 1200°, whereby the hydride is completely decomposed and the volatilised barium is condensed on a polished steel tube cooled by circulating water placed inside where the vapours are being liberated. The metal so obtained assayed 99·5 p.c. barium and was free from hydrogen.

A very convenient laboratory method for preparing small quantities of barium, also due to Guntz, is to heat barium oxide with one-tenth its weight of metallic aluminium at 1200° in a vacuum. The metal condenses in the cooler part of the tube and assays as much as 98·8 p.c. barium.

Matignon (Compt. rend. 150, 1378) has obtained barium by heating the oxide (3 mols.) with silicon (1 atom.) in a vacuum, in a steel tube, at 1200°. The metal distils off and condenses in the cooler part of the tube, the reaction being—

$$3BaO+Si=BaSiO_3+2Ba-37 \text{ cals.}$$

The silicon can be replaced by ferro-silicon containing 95 p.c. silicon.

The preparation of the metal by electrolysis of the fused oxide or chloride does not appear to be attended with success; sub-salts are formed, and the current passes without further action (Z. Electroch. 9, 291).

Properties.—Barium when absolutely pure is a silver-white metal with a density of 3·78. It is slightly harder than lead. It melts at about 850° and commences to volatilise at 950°. Barium oxidises rapidly in air, yielding principally the monoxide; the powder easily takes fire spontaneously. Guntz states that molten barium attacked all the metals he tried, iron and nickel being the most resistant. Barium decomposes water and alcohol in the cold, yielding in the latter case barium ethoxide.

Oxides of barium. Three oxides of barium are known—barium suboxide Ba_2O, barium oxide or baryta BaO, and barium peroxide BaO_2.

Barium suboxide Ba_2O is obtained, according to Guntz (Compt. rend. 143, 339), by heating the protoxide with magnesium or barium to a temperature of 1100°. It is a black mass which decomposes water.

Barium oxide, protoxide, monoxide, or baryta, BaO, is the oxide formed when the metal burns in air. It is more readily obtained by heating (1) the nitrate or (2) the carbonate of barium.

(1) Barium nitrate heated progressively, fuses, then decomposes with the liberation of nitric fumes and much frothing leaving a porous mass of barium oxide.

(2) The carbonate may also be converted into barium oxide by exposing it to the strongest heat of a forge fire; but the last traces of carbonic acid are only expelled with difficulty. However, at an ordinary white heat, this may be accomplished by mixing the carbonate with one-tenth of its weight of lampblack or charcoal and making into a thick paste with oil or tar, carbonic oxide being evolved, thus:

$$BaCO_3+C=BaO+2CO.$$

The mixture should be heated in an earthen crucible lined with lampblack and fitted with a tight cover; on the large scale witherite is thus converted into baryta for use in separating crystallised sugar from molasses. In a second baryta-manufacturing process a mixture of the carbonates of barium and calcium is ignited in a current of aqueous vapour.

(3) On the small scale, baryta may be easily obtained by heating barium iodate, which readily gives up all its iodine, together with five-sixths of its oxygen, without fusing or frothing:

$$Ba(IO_3)_2=BaO+I_2O_5.$$

Barium oxide as prepared by the above methods is generally a greyish-white friable mass of specific gravity 4·7–5·5. Brügelmann (Annalen, [2] 4, 277), by heating barium nitrate in a porcelain flask, obtained minute crystals of BaO belonging to the regular system, of sp.gr. 5·722. He found later that by heating the oxide in a clay or graphite crucible he obtained needles belonging to the hexagonal system sp.gr. 5·32, but if heated in a platinum crucible the oxide is obtained in cubic forms, sp.gr. 5·74. It is therefore dimorphous (Zeitsch. anal. Chem. 29, 127). It is only just melted even by the heat of the oxyhydrogen blowpipe; but in the electric furnace it may be readily liquefied and volatilised. The liquid on cooling yields a crystalline mass (Moissan, Ann. Chim. Phys. [7] 4, 139); it is a non-conductor of electricity, but in presence of mercury may be electrolysed into barium and oxygen. BaO is strongly alkaline, caustic, and poisonous. Fluorine attacks it in the cold, liberating oxygen, the mass becoming incandescent. Dry chlorine has little or no action on the perfectly anhydrous baryta. It is deoxidised by potassium at a red heat, and slakes with water, forming barium hydrate $Ba(OH)_2$ with such energy that the whole mass becomes incandescent provided the amount of water be not too large. It rapidly absorbs moisture from the air. It unites with methyl and ethyl alcohols, forming the compounds $BaO,2CH_4O$ and $BaO,2C_2H_6O$. Heated in the vapour of carbon disulphide, it forms barium carbonate and barium sulphide:

$$3BaO+CS_2=BaCO_3+2BaS.$$

It dissolves readily in dilute nitric and hydrochloric acids, but with most other acids forms insoluble salts. When vapour of sulphuric anhydride is passed over it, heated to low redness in a glass tube, formation of barium sulphate $BaSO_4$ occurs with incandescence.

Barium peroxide or dioxide BaO_2 is formed when anhydrous baryta is heated to a dull red heat in a stream of oxygen or of air freed from carbonic acid. Barium hydroxide may be similarly converted into the peroxide, but less readily, as it fuses below the temperature of absorption of oxygen; but the absorption may be rendered rapid by mixing the hydroxide with lime or magnesia which prevents fusion and keeps the mass porous. Peroxide of barium may also be obtained by sprinkling red-hot baryta with four times its weight of powdered potassium chlorate in successive small portions; the potassium chloride simultaneously formed may be washed out with water, leaving the peroxide in the form of a hydrate.

The peroxide obtained by these means is not pure, being contaminated with a little unconverted barium oxide, iron, silica, and other substances derived from the preparing vessels. In order to purify it the finely powdered crude product is gradually added to an excess of dilute hydrochloric acid, avoiding any considerable rise of temperature; the crude substance dissolves, forming barium chloride and peroxide of hydrogen. The solution is filtered from insoluble matters and treated with baryta water until the silica and ferric oxide, together with a little hydrated barium peroxide, regenerated by action of the peroxide of hydrogen upon the barium hydroxide, are precipitated. The liquid is again filtered and then supersaturated with baryta. By this means the whole of the peroxide of hydrogen regenerates barium peroxide, which is precipitated in minute prisms or laminæ of the hydrate $BaO_2,8H_2O$, in which condition the peroxide is best preserved, and is a suitable form for use in the preparation of peroxide of hydrogen. On drying at 130° or at ordinary temperatures *in vacuo* it is converted into pure anhydrous barium peroxide.

The preparation of barium peroxide in the wet way always yields the octohydrate when more than one molecule of baryta is present per molecule of H_2O_2. Above 60° it is formed, whatever the composition of the solution. Below 40° the di-peroxyhydrate $BaO_2,2H_2O_2$ is obtained from solutions containing much H_2O_2. A compound BaO_2,H_2O_2 may be obtained between 30° and 60° (Zeitsch. Anorg. Chem. 89, 405).

Barium peroxide is a grey, impalpable powder, slightly more fusible than the monoxide. The temperature of dissociation depends upon the pressure. According to Le Chatelier (Compt. rend. 115, 654), the figures are as follows:—

Temp. C.°	520	555	650	670	720	735	750	775	785	790
Press. mm.	20	25	65	80	210	260	340	510	620	670

These pressures vary according to the degree of decomposition being highest at the commencement of the operation. Brin's method of preparing oxygen depends upon the above physical factors. The spongy protoxide of barium prepared as indicated above is placed in thin beds in iron retorts heated by special furnaces. The temperature is maintained as constant as possible between 500° and 600°. Air which has been freed from moisture and carbon dioxide by passing first over quicklime and then over caustic soda is forced by pumps through the retorts whereby the BaO is converted to BaO_2. The residual nitrogen is allowed to escape into the atmosphere. When the peroxidation is complete a set of valves places the retorts in connection with the exhaust pumps, the reduction of pressure causing liberation of oxygen. The first portions are allowed to escape until the pressure measures 65 cm. mercury, another set of valves then comes into play and automatically connects the retorts with the gasometer. The oxygen obtained is 97 to 98 p.c. pure. Barium peroxide is used in the preparation of hydrogen peroxide or dissolved in accidulated water as a bleaching agent.

Peroxide of barium is decomposed by sulphuretted hydrogen at ordinary temperatures, and when heated in a current of carbonic oxide it becomes white hot. It becomes incandescent when heated in sulphur dioxide. When treated with strong sulphuric acid at a temperature exceeding 70°, oxygen is given off; at lower temperatures the oxygen is mixed with ozone. When the peroxide is mixed with acidulated water in presence of oxide of silver, peroxide of manganese, or peroxide of lead, oxygen is evolved both from the peroxide of barium and from the other oxide. A small quantity of a silver compound is capable of decomposing a large quantity of barium peroxide, but iodine decomposes an exactly equivalent quantity:

$$BaO_2+I_2=BaI_2+O_2.$$

The amount of active oxygen in BaO_2 may be determined by adding a known quantity of the peroxide to pure hydrochloric acid, then potassium iodide free from iodate together with excess of bicarbonate of soda, and titrating the liberated iodine with a standard solution of sodium thiosulphate. It may also be estimated by titrating an acidulated solution with standard potassium permanganate (Bertrand, Bull. Soc. chim. [2] 33, 148).

Barium hydroxide, *Hydrate of Baryta*, or *Caustic Baryta* $Ba(OH)_2$ or $BaO{\cdot}H_2O$, is formed, with great evolution of heat, when water is added to anhydrous baryta (barium oxide):

$$BaO+H_2O=Ba(OH)_2.$$

A hot concentrated solution of equivalent quantities of barium nitrate and sodium or potassium hydroxide deposits, on cooling, crystals of barium hydroxide. Soda is usually employed, of sp.gr. 1·10–1·15, and the crystals obtained are freed from mother liquor by draining, or better, by means of a centrifugal machine.

Commercial caustic baryta is prepared on the large scale by igniting the native sulphate or heavy spar with coal or charcoal, whereby an impure barium sulphide is obtained, and heating this is earthenware retorts into which a current of moist carbonic acid is passed, thus converting it into carbonate:

$$BaS+CO_2+H_2O=BaCO_3+H_2S.$$

Superheated steam is then passed over the heated carbonate, when the following decomposition takes place:—

$$BaCO_3+H_2O=Ba(OH)_2+CO_2.$$

According to R. Heintz (Chem. Zeit. 1901, 199), only the carbonate is used to any extent. The calcination is conducted in specially constructed furnaces lined with basic material and heated with producer gas. The product contains 95 p.c. BaO. The same author reviews the methods that have been suggested for the manufacture of baryta from barytes, and considers them too costly for the production of a cheap commercial oxide.

Marino (Gazz. chim. ital. 43, 416) has shown that the reduction of barium sulphate to sulphide is effected by reducing gases, especially water gas, more readily than with the use of coal, the reduction occurring at 525°–540°. In practice 600°–625° is used, and a yield of 95–98 p.c. was obtained in an experimental furnace. Baryta is then prepared by the electrolysis of a solution of barium sulphide by Brochet and Ransome's process, a diaphragm of high resistence being employed in all cases. The best results are obtained with copper electrodes and a solution containing 20 p.c. of BaS. The barium hydrate at the anode increases as long as the concentration does not fall below 5 p.c., and in concentrated solutions, at 70°–80° amounts, after 24 hours, to 13 grms. per litre. Formation is due to interaction of hydroxyl ions with the BaS.

Caustic baryta crystallises from water in large, transparent, colourless, quadratic prisms capped by pyramids. The crystals $Ba(OH)_2,8H_2O$ are isomorphous with the corresponding strontium compound. They dissolve in 20 parts of water at 15°, and in 2 parts of boiling water. The aqueous solution known as baryta water is highly caustic and of strong alkaline reaction, rapidly becoming covered with a film of carbonate owing to absorption of atmospheric carbonic acid; hence it is frequently used in the determination of the amount of carbonic acid contained in the air. On exposure to air the crystals fall to a white powder, with loss of seven molecules of water. De Forcrand (Compt. rend. 103, 59) isolated the hydrate $Ba(OH)_2,H_2O$ by allowing the compound $BaO,2CH_3O+2H_2O$ to evaporate over sulphuric acid *in vacuo*. H. Lescœur (Compt. rend. 96, 1578) shows that at 100° $Ba(OH)_2,H_2O$ has a tension of dissociation of 45 mm., and that this hydrate is completely converted to $Ba(OH)_2$ when heated to 100° *in vacuo*. Lescœur also proves that the dissociation tension of $Ba(OH)_2,8H_2O$ is 213 mm. at 75°, so that at this temperature all three hydrates of BaO may exist simultaneously.

$Ba(OH)_2$, when heated alone, is only reduced to baryta above a red heat; if not heated above redness, it re-forms, on cooling, a crystalline mass of $Ba(OH)_2$, but when heated in a current of air it takes up oxygen and is converted into peroxide of barium with loss of water; when heated in a current of carbonic acid it also loses water and is converted into barium carbonate:

$$Ba(OH)_2+O=BaO_2+H_2O.$$
$$Ba(OH)_2+CO_2=BaCO_3+H_2O.$$

Baryta has until recently been used in the processes of sugar-refining, inasmuch as it forms the compound $C_{12}H_{22}O_{11}BaO$ with cane-sugar, which, when treated with carbonic acid gas, is decomposed into insoluble barium carbonate and sugar, hence affording a means of separating the pure sugar from the molasses; but as strontium hydrate acts in a similar manner, and is not poisonous, it has been substituted for baryta in sugar-refining.

Hydrated barium peroxide. Schöne has shown (Ber. 13, 803) that only one hydrate of BaO_2 exists, containing 8 molecules of water, $BaO_2,8H_2O$. This hydrate is precipitated in crystalline scales when peroxide of hydrogen is added to concentrated solutions of barium hydroxide. It is slightly soluble in cold water, but decomposes in boiling water, forming $Ba(OH)_2$ and evolving oxygen.

Barium subchloride BaCl is obtained (Guntz, Bull. Soc. chim. [3] 29, 490) when equal amounts of $BaCl_2$ and Ba are heated together *in vacuo* at 850°. The fragments of $BaCl_2$ absorb the molten barium without change, and are microcrystalline. The material so obtained is not pure. It decomposes water. By using Na, a definite compound NaClBaCl can be obtained. BaCl appears to be formed when electrolysing fused $BaCl_2$.

Barium chloride $BaCl_2$. Crystallised (*terra ponderosa salita*) $BaCl_2,2H_2O$. Barium chloride may be prepared either from witherite, the native carbonate, or from heavy-spar, the native sulphate. The witherite is dissolved in dilute hydrochloric acid and the solution allowed to stand some time in contact with excess of the carbonate, which is added to precipitate iron and other foreign metals present in the mineral; the rapidity of precipitation is much increased by the addition of a little baryta water. The filtered liquid is then neutralised with hydrochloric acid, and the salt crystallised out and purified by recrystallisation.

From the native sulphate barium chloride may be prepared in two ways:

(1) By heating the sulphate in a crucible with powdered coal and decomposing a filtered solution in water of the barium sulphide formed with hydrochloric acid: $BaS+2HCl=BaCl_2+H_2S$.

Excess of hydrochloric acid is added, and the liquid boiled till free from sulphuretted hydrogen; it is then filtered, cooled, and evaporated to the crystallising point.

(2) By heating a mixture of 100 parts finely powdered heavy-spar, 40 parts of charcoal, 20 parts of limestone, and 50 parts of calcium chloride to a red heat in a reverberatory furnace, by which barium chloride and calcium sulphide are formed. The mass is lixiviated with water, when the barium chloride is dissolved out, leaving an insoluble calcium oxysulphide formed by the union of the sulphide with the oxide of calcium produced by ignition of the limestone.

Commercial barium chloride generally contains small quantities of strontium and calcium chlorides, together with traces of the chlorides of iron, aluminium, copper, and lead. Washing the crystals with alcohol removes both the strontium and calcium chlorides, whilst calcium chloride may also be removed by digesting with barium carbonate suspended in water, when the calcium chloride becomes converted to carbonate, or more rapidly by adding baryta water and passing carbonic acid gas into the liquid. Digestion with barium carbonate also precipitates the sesquioxides of iron and alumina. Lead and copper may best be removed by the addition of a little barium sulphide.

Barium chloride may be recovered from mixtures of chlorides of the alkalis and alkaline earths by treating the concentrated liquor with a hot saturated solution of salt, when on cooling a mixture of barium and sodium chlorides crystallises out; by treating a cold saturated solution of this mixture with twice its volume of hydrochloric acid, barium chloride is precipitated (Dingl. poly. J. 250, 91).

Barium chloride crystallises from aqueous solution with two molecules of water $BaCl_2,2H_2O$ in transparent, colourless, rhombic tables; sp.gr. 2·66–3·05. The crystals decrepitate when heated. They have an unpleasant, bitter, sharply saline taste, exciting nausea, and are very poisonous.

One hundred parts of water at 0° dissolve 32·62 parts of anhydrous barium chloride, and 0·2711 part for every degree above 0°; 100 parts of water at 15·6° dissolves 43·5, and at 105·5° 78 parts of the crystallised chloride. One part of crystallised barium chloride at 18·1° dissolves in 2·257 parts of water to form a solution of sp.gr. 1·28251 (Karsten). A solution saturated at 8° has a sp.gr. of 1·270 (Anthon).

Barium chloride is almost insoluble in strong hydrochloric acid, so that it is precipitated from its solutions by hydrochloric acid, and a few drops of the acid reduces the solubility considerably. Hot absolute alcohol dissolves only $\frac{1}{400}$ part of the crystals; but according to Fresenius, 1 part of the salt dissolves in 8108 parts of alcohol of 99·3 p.c. at 14°, and in 4857 parts of the same alcohol at its boiling point.

The crystals are not efflorescent, but give up the whole of their water at 100°, leaving a white mass of the anhydrous salt, which melts at a red heat, forming a translucent mass on cooling; the crystals are optically biaxial and positive. Specific gravity of the anhydrous chloride is given by various observers as 3·70 to 4·15. Hans Winter (Diss. Leipzig. 1913, 1) gives the following constants, m.p. 958°, sp.gr. 3·789. When heated in a current of steam it evolves hydrochloric acid below its fusing point.

Calcium and barium chlorides form the double salt $CaCl_2BaCl_2$ (m.p. 631°), but no mixed crystals. Barium and strontium chlorides form a complete series of regular (β) mixed crystals, which on cooling are transformed to (α) crystals (monoclinic). The two series correspond with the α and β forms of $BaCl_2$, which coexist in equilibrium at 922°. The freezing-point curve shows a minimum at 847°, at which point 30 mols. p.c. $BaCl_2$ are present. The double chlorides $2KCl,SrCl_2$ and $2KCl,BaCl_2$ are isomorphous and rhombic.

A concentrated solution of barium chloride is decomposed by sodium or potassium nitrate, forming barium nitrate and a chloride of the alkali-metal. With glycocol $CH_2(NH_2)\cdot COOH$ it forms a crystalline compound, and also acts upon blood as a preventive of putrefaction and coagulation.

Barium chloride is extensively used as a reagent, especially for the detection and estimation of sulphuric acid. It is also used for the preparation of artificial sulphate or 'permanent white,' and for preventing the incrustation of steam boilers by decomposing the gypsum of hard waters.

Barium oxychloride. André (Compt. rend. 93, 58) obtained an oxychloride of barium by adding 60 grams of $Ba(OH)_2$ to 200 grams of crystallised barium chloride, and boiling the mixture with 500 grams of water, filtering, and allowing to cool, when nacreous lamellæ, to which he ascribed the formula $BaCl_2\cdot BaO,5H_2O$, separated out (Compt. rend. 98, 572). Beckmann (J. pr. Chem. [2] 27, 126) also obtained nacreous plates by similar means to which he gave the formula $BaCl(OH),2H_2O$. These plates lose $\frac{4}{5}$ths of their water at 120° and the remaining fifth at the fusing-point by prolonged heating in a stream of hydrogen. This oxychloride is readily decomposed by water or alcohol.

Barium chlorite $Ba(ClO_2)_2$ may be obtained absolutely free from chloride by the action of a mixture of chlorine dioxide and carbon dioxide free from chlorine on barium peroxide suspended in hydrogen peroxide. The decomposition of barium chlorite takes place according to the equation—

$$Ba(ClO_2)_2=BaCl_2+2O_2+48{\cdot}6 \text{ cals.}$$

From this follows the equation—

$$Ba+Cl_2+2O_2=Ba(ClO_2)_2(\text{solid})+148 \text{ cals.}$$

and

$$BaCl_2+2O_2=Ba(ClO_2)_2-48{\cdot}6 \text{ cals.}$$
$$Ba(ClO_2)_2+O_2=Ba(ClO_3)_2+22{\cdot}8 \text{ cals.}$$
$$Ba(ClO_3)_2+O_2=Ba(ClO_4)_2+30{\cdot}2 \text{ cals.}$$

Consequently in compounds containing chlorine in different degrees of oxidation the formation is the less endothermic and the more exothermic the higher the degree of oxidation (Gazz. chim. ital. 45, 161).

Barium chlorate $Ba(ClO_3)_2$. Dry $Ba(OH)_2$ does not absorb chlorine, but in presence of water it rapidly takes it up, forming first hypochlorite and chloride, the former of which breaks up into chlorate and chloride

$$6BaO+6Cl_2=5BaCl_2+Ba(ClO_3)_2$$

(Konigel-Wiesberg, Ber. 12, 346).

As it is difficult to separate from the chloride, the chlorate is best prepared by neutralising a solution of chloric acid with barium carbonate and evaporating to the crystallising point. It crystallises in colourless monoclinic prisms with 1 molecule of water, soluble in 4 parts of cold and less than 1 part of boiling water.

Barium chlorate is also slightly soluble in alcohol, and the alcoholic solution burns with a green flame.

If strongly heated fused barium chlorate be plunged into a jar of coal gas, a brilliant combustion of the carbon and hydrogen contained in the coal gas occurs at the expense of the oxygen of the chlorate.

Barium perchlorate $Ba(ClO_4)_2,4H_2O$ is readily formed by neutralising perchloric acid with barium hydrate or carbonate. It crystallises from the solution in long deliquescent prisms very soluble in water.

Barium bromide $BaBr_2$. Crystallised

$$BaBr_2,2H_2O.$$

This salt is prepared by saturating baryta water or barium carbonate or sulphide with hydrobromic acid; or by decomposing the sulphide with free bromine, sulphur being precipitated.

The most convenient method is to bring together under water 12·5 parts of bromine and 1 part of amorphous phosphorus, by which a solution of hydrobromic and phosphoric acids is formed, which is neutralised with barium carbonate rendered alkaline by baryta water. The insoluble barium phosphate may then be filtered off and the bromide obtained by evaporation and crystallisation.

Barium bromide is very soluble in water, and crystallises with difficulty; it is isomorphous with the chloride, but unlike the latter salt is soluble in strong alcohol. It loses one molecule of water at 75°, and the second at 120° (Beckmann, J. pr. Chem. [2] 27, 126), m.p. of anhydrous salt 847°.

Barium oxybromides. Two oxybromides have been prepared by Beckmann (*l.c.*)

$BaBr(OH),2H_2O$ resembles the corresponding oxychloride. $BaBr(OH),3H_2O$ was obtained by adding alcohol to mixed solutions of $BaBr_2$ and $Ba(OH)_2$.

Barium iodide BaI_2. Anhydrous, sp.gr. 4·917, it forms several hydrates with 7,6,2,1 molecules of water. Barium iodide is formed when hydriodic acid gas is passed over baryta at a red heat, a violent action occurring attended with incandescence. It is generally prepared by mixing barium monosulphide with a saturated solution of iodine in alcohol as long as sulphur is precipitated; the filtrate is then boiled rapidly to near dryness, redissolved in a little water and again evaporated, this time to dryness, preventing the access of air as much as possible by performing the operation in a glass bolt head. On redissolving the mass in hot water and allowing to cool, slender needles separate out of the composition $BaI_2,7H_2O$ (Croft, Gazz. chim. ital. 1856, 125; Thomsen, Ber. 10, 1343).

These crystals are very deliquescent and readily soluble in alcohol. They lose 6 molecules of water at 125°, and the remainder at 150° (Beckmann, J. pr. Chem. [2] 27, 126). They decompose slowly at ordinary temperatures, and quickly when warmed, giving off violet vapours of iodine. Commercial barium iodide crystallises at the ordinary temperature in large hexagonal prisms, apparently isomorphous with $SnCl_2,6H_2O$. They melt in their water of crystallisation at 25·7° (Centr. Min. 1918, 105).

The double iodide of barium and mercury has a sp.gr of 3·588 higher than that of Thoulet's solution, and may be of use for petrographical purposes (Rohrbach, Jahrb. Min. 1883, 2, Mem. 186).

Barium oxyiodide. Beckmann (J. pr. Chem. [2] 27, 126) prepared an oxyiodide of barium of the formula $BaI(OH),4H_2O$ which crystallises in short thick needles.

Barium iodate $Ba(IO_3)_2$ is largely used for the preparation of iodic acid, and is obtained as a white granular precipitate by adding potassium iodate to barium chloride.

It is soluble in 3000 parts of cold and 600 parts of boiling water. It dissolves in hot nitric acid, and crystallises out on cooling in bright, glittering, monoclinic prisms isomorphous with the chlorate. Hydrochloric acid dissolves it with evolution of chlorine.

Barium periodate. By passing iodine vapour in a current of dry air over heated oxide of barium a basic periodate of the formula $Ba_5I_2O_{12}$ or $Ba(IO_4)_2 \cdot 4BaO$ is formed. The same basic periodate is formed when barium iodate is heated to a high temperature:

$$5Ba(IO_3)_2 = Ba_5I_2O_{12} + 4I_2 + 9O_2$$

or on heating barium iodide in a current of air until no more iodine is given off:

$$5BaI_2 + 6O_2 = Ba_5I_2O_{12} + 4I_2.$$

Hence Sugiura and Cross (J. Chem. Soc. 1879, 118) conclude that $Ba_5I_2O_{12}$ is the most stable combination of barium, iodine, and oxygen.

Barium fluoride BaF_2 (m.p. 1289°), is obtained by neutralising hydrofluoric acid with barium hydroxide or recently precipitated carbonate; or by precipitating a solution of barium nitrate with sodium or potassium fluoride. It forms a white, granular, crystalline powder, sparingly soluble in water, but readily soluble in nitric, hydrochloric, or hydrofluoric acids. It crystallises in the cubic system.

It combines with fluorides of silicon and boron, forming the compounds $BaF_2 \cdot 2SiF_4$ barium silicofluoride and $BaF_2 \cdot 2BF_3$. The former is precipitated by adding hydrofluosilicic acid to soluble barium salts as a crystalline precipitate totally insoluble in alcohol, and serves as a means of separating barium from strontium and calcium, which are not precipitated by hydrofluosilicic acid.

Barium fluoride forms a crystalline compound with the chloride of barium $BaCl_2 \cdot BaF_2$ when a solution of barium chloride is mixed with one of sodium or potassium fluoride; this double compound is more stable than the fluoride itself, and remains as a granular mass on evaporation of the solution. The crystals are tetragonal in habit, and optically negative, m.p. 1008°, sp.gr., 5·931.

Barium carbide BaC_2 was first obtained by Maquenne (Ann. Chim. Phys. (6) 28, 259) by heating a mixture of the carbonate and carbon with magnesium or by the action of carbon on the amalgam in an atmosphere of hydrogen at a red heat. Moissan (Compt. rend. 118, 683) obtained it in a pure crystalline condition by heating a mixture of the carbonate or the oxide with carbon in an electric furnace. Its specific gravity is 3·75, and it possesses properties similar to CaC_2, but is more fusible.

Barium carbonate $BaCO_3$. The native carbonate was first noticed to occur at Leadhills in Scotland, in 1783, by Withering, and hence received the name *witherite*. It is found in many places in England, specially fine crystals being met with at Fallowfield in Northumberland: it is also found in Silesia, Hungary, Styria, Russia, South America. Witherite crystallises in the rhombic system isomorphous with aragonite. It occurs also in globular, tuberose, and botryoidal forms; more frequently massive. Sp.gr. 4·29–4·35; hardness 3–3·75.

Knop (Landw. Versuchs-Stat. 17, 65) found 0·02 p.c. of barium carbonate in Nile mud from Minich and Achmin; and Dworzack (Landw. Versuchs-Stat. 17, 65) found baryta in the ash of the wheat grown thereon. *Alstonite* $(BaCa)CO_3$ contains barium and calcium in varying proportions, and is isomorphous with witherite. *Baryto-calcite* $BaCO_3 + CaCO_3$ crystallises in the monoclinic system.

Boeke (Jahrb. Min. 9–10) shows by heating barium carbonate under pressure of carbon-dioxide, that it undergoes two reversible transformations. At 811° the ψ form (witherite, orthorhombic and pseudo-hexagonal) passes to the β form (hexagonal), and at 982° to the α form (cubic), m.p. about 1740°. The system barium carbonate-calcium carbonate (represented by the minerals alstonite and barytocalcite) give iso-dimorphous mixed crystals with a eutectic at 1139° and 52½ mol. p.c. $CaCO_3$. Up to 30 mol. p.c. $CaCO_3$ the orthorhombic alstonite is the stable form, but with more calcium carbonate, this is replaced by trigonal baryto-calcite. Monoclinic baryto-calcite is not present in the fusions.

Barium carbonate is rapidly formed when baryta, hydrated or anhydrous, is exposed to the atmosphere. When BaO is heated in CO_2 it absorbs the gas, becoming incandescent; the basic carbonate being formed (Raoult, Compt. rend. 92, 1, 110).

It is readily prepared by precipitating aqueous solutions of the nitrate or chloride with ammonium carbonate, filtering, and washing with hot water; or by igniting a mixture of 10 parts powdered heavy-spar, 2 parts charcoal, and 5 parts pearl ash (potassium carbonate). Potassium sulphide and barium carbonate are obtained and may be separated by water. The impure carbonate thus produced may be used to prepare other salts of barium, but these salts will contain iron.

Artificial barium carbonate is a dense soft white powder, poisonous, and hence used for destroying rats. It is very sparingly soluble in water, slightly soluble in water containing carbonic acid, owing to the formation of an acid carbonate which is stable only in solution. It dissolves readily in ammonium chloride, nitrate, and succinate, and when boiled with ammonium chloride is totally decomposed, forming ammonnium carbonate and barium chloride.

The solubility of $BaCO_3$ in water has been determined by Missenberger (Zeitschr. physikal. Chem. 88, 257), and also in water containing small quantities of sodium hydroxide, which represses the hydrolysis and so furnishes a lower and more accurate value for the solubility. The minimum solubility is found in aqueous solutions containing $1 \cdot 25 \times 10^{-5}$ mols. of sodium hydroxide. The following values were obtained (1) for pure water at 13°, $1 \cdot 62 \times 10^{-3}$; 18°, $1 \cdot 72 \times 10^{-3}$; 22°, $1 \cdot 83 \times 10^{-3}$; 27°, $1 \cdot 96 \times 10^{-3}$; 33°, $2 \cdot 14 \times 10^{-3}$; 37°, $2 \cdot 28 \times 10^{-3}$ mols. per litre, and (2) true values calculated from experimental results in faintly alkaline solutions at 14°, $4 \cdot 32 \times 10^{-4}$; 18°, $4 \cdot 57 \times 10^{-4}$; 23°, $4 \cdot 89 \times 10^{-4}$; 27°, $5 \cdot 22 \times 10^{-4}$; 32°, $5 \cdot 69 \times 10^{-4}$; 38°, $6 \cdot 27 \times 10^{-4}$ gram mol. per litre.

It is not decomposed at a strong red heat, but at 1361° it fuses with loss of carbon dioxide; the tension of CO_2 emitted at 1100° is 20 mm.; at 1600° dissociation is complete. The decomposition is much more easily effected in presence of carbon, being complete at 1450°. It is decomposed by steam at a red heat, and very easily if mixed with an equal weight of chalk or slaked lime.

The artificial carbonate is of considerable use in chemical analysis.

Barium nitride Ba_3N_2. Maquenne (Bull. Soc. chim. [3] 7, 368) obtained this compound by passing nitrogen into a tube containing a 25 p.c. amalgam at a red heat. Guntz and Mentrel (*ibid.* (3) 29, 581) obtained it by heating barium ammonium at 430°. So obtained it is a light porous material of a canary-yellow colour. It decomposes water in the cold, giving ammonia and $Ba(OH)_2$.

The pure nitride and hydride are readily obtained by heating the metal in the respective gases. When the nitride is heated in a current of hydrogen a compound having the formula $Ba_3N_2H_4$ is formed, but the product is impure since the compound reacts even at relatively low temperatures with hydrogen according to the equation

$$Ba_3N_2H_4+H_2=3BaH_2+N_2$$

When hydrogen is passed over the heated impure nitride ammonia is formed. BaH_2 which is thereby produced is readily transformed back to the nitride by the action of nitrogen, so that a process is given for the fixation of nitrogen (Monatsh. 34, 1685).

Barium ammonium is formed by the action of ammonia gas on barium or barium amalgam below 28°; but it is best prepared by dissolving barium in dry liquid ammonia at −50°, when it forms a dark-blue oily liquid immiscible with the liquid ammonia. The compound is somewhat indefinite, but a body having the formula $Ba(NH_3)_6$ appears to exist.

Barium amide $Ba(NH_2)_2$ is obtained by heating barium ammonium to 60° or by passing ammonia over barium at 280° C.

When a barium salt and excess of potassamide are allowed to interact in liquid ammonia solution a white insoluble precipitate of potassium ammonobariate $BaNK,2NH_3$, or $Ba(NH_2)_2,KNH_2$, is produced. The strontium and calcium salts may be prepared in the same way (J. Amer. Chem. Soc. 37, 2295).

Barium nitrite $Ba(NO_2)_2,H_2O$ is prepared by heating the nitrate, dissolving in water, and precipitating any baryta formed by passing a stream of carbon dioxide through the solution, adding alcohol to the filtrate to precipitate the unreduced nitrate, and evaporating to the crystallising point. Or by passing nitrous vapours into baryta water, evaporating to dryness, digesting in a small quantity of water (not sufficient to dissolve the nitrate) and crystallising. It is most readily prepared pure by adding barium chloride to a boiling solution of silver nitrite, filtering off the silver chloride, and evaporating.

It is permanent in the air, readily soluble in water or alcohol, and crystallises in colourless prisms, either needle-shaped or, according to Fischer, thick short prisms of 71½°.

Barium nitrate $Ba(NO_3)_2$. A native barium nitrate has been discovered in Chile in the form of colourless octahedra, occasionally twinned like spinel (Groth, Jahrb. Min. 1883, 1, Ref. 14).

Barium nitrate is prepared on the large scale either by dissolving the native carbonate (witherite) or the crude sulphide in dilute nitric acid, or by mixing hot saturated solutions of barium chloride and sodium nitrate. On cooling, the larger portion of the barium nitrate crystallises out, and the evaporation of the mother liquors yields the remaining portion.

Barium nitrate crystallises in lustrous, colourless, regular octahedra, frequently modified by faces of the cube, of sp.gr. 3·2. The crystals are permanent in the air, decrepitating when heated, and melting at 595·53° (Carnelley 597°). At a red heat the salt decomposes, evolving oxygen, nitrogen, and nitrogen peroxide, and leaving a residue of pure baryta. It detonates slightly with combustible bodies, and decomposes with a yellowish light when thrown upon the fire. It is largely used in pyrotechny for giving green-coloured lights, especially for the preparation of green fire; and for the manufacture of *saxifragin*, an explosive mixture of 76 parts of barium nitrate, 2 parts of nitre, and 22 parts of charcoal.

It dissolves in water, producing a slight depression of temperature; 100 parts of water dissolve 5·2 parts of barium nitrate at 0°, 9·2 at 20°, 17·1 at 50°, and 32·2 at 100°. It is less soluble in dilute nitric acid; hence a second crop of crystals may be obtained from cooled saturated solutions on addition of a little nitric acid. It is quite insoluble in concentrated nitric acid and in alcohol.

Hirzel (Zeitsch. f. Pharm. 1854, 49) obtained a hydrate $Ba(NO_3)_2,2H_2O$ from a solution cooled below 12°. Berry (Chem. News, 44, 190), by saturating the same water with barium and strontium nitrates, introducing a crystal of $Sr(NO_3)_2,4H_2O$, and evaporating over sulphuric acid *in vacuo*, obtained crystals containing 17 p.c. of a hydrated barium nitrate isomorphous with the strontium compound. On account of the great electro affinity of nitrion (nitrate ion), the formation of double nitrates is found to occur in few cases, and with one exception (the double nitrate of barium and potassium) are formed only when one of the metals has a valency greater than 2. The unexpected formation of the double nitrate of potassium and barium was first observed by Wallbridge (Amer. Chem. J. 30, 154), whose analysis showed it to be anhydrous and to have the formula $2KNO_3,Ba(NO_3)_2$. Foote showed (Amer. Chem. J. 32, 251) that the double salt can form at 25° under a moderately wide range of conditions, as, for example, from solutions containing 15 to 27 p.c. KNO_3, and from 6 to 2 p.c. $Ba(NO_3)_2$. The salt cannot be recrystallised. Only one well-defined basic nitrate $Ba_2N_2O_7$ is known, and this forms several hydrates.

Barium monosulphide BaS is obtained in a pure state by passing sulphuretted hydrogen over heated baryta as long as water is formed. Veley (Chem. Soc. Trans. 1886, 369) prepared pure crystals of the hydrate of barium hydroxide $Ba(OH)_2,8H_2O$, and heated them at 80° in a current of hydrogen until they attained the constant composition $Ba(OH)_2,H_2O$, when a stream of sulphuretted hydrogen was passed over them, yielding pure BaS and water:

$$Ba(OH)_2,H_2O+H_2S=BaS+3H_2O$$

It may also be prepared by passing carbon disulphide over red-hot baryta, or by reducing powdered barium sulphate in a stream of hydrogen.

On the manufacturing scale it is prepared by roasting 100 parts of heavy-spar with 20 parts of coal slack or charcoal. If charcoal is used, a thorough mixture must be effected, as the reaction is otherwise very imperfect, owing to the non-fusibility of the mass. If the slack of bituminous coal is used, the 'caking' supplies a carbonaceous material which readily permeates the mass and ensures complete reduction. The admixture of resin, oil, or sawdust is also advantageous, and the asphalt of gasworks is a capital reducing material, as the hydrogen contained in it prevents the formation of polysulphides of barium. The mass thus obtained contains excess of carbon and some undecomposed sulphate, but the barium sulphide may be extracted by treating with hot water.

Another method is to heat a mixture of 100 parts heavy-spar, 200 of common salt, and 15 parts charcoal powder in a reverberatory furnace, the salt being added to assist fusion.

Barium sulphide forms a white mass of hepatic odour and alkaline taste, soluble in water, forming a mixture of hydrate and sulphydrate:

$$2BaS+2H_2O=Ba(SH)_2+Ba(OH)_2$$

When exposed to the air it becomes converted into carbonate with evolution of sulphuretted hydrogen, owing to absorption of moisture and carbonic acid. When heated to redness in presence of aqueous vapour, it is converted into barium sulphate with elimination of hydrogen. It is decomposed by hydrochloric and nitric acids with formation of the chloride and nitrate and elimination of sulphuretted hydrogen. Chlorine, bromine, and iodine decompose it with formation of chloride, bromide, and iodide, and deposition of sulphur.

The phosphorescent material known as 'Bolognian phosphorus' is a sulphide of barium obtained by heating 5 parts of precipitated barium sulphate with 1 part of powdered charcoal over a gas flame for half an hour, and then heating for ten minutes over the blowpipe; it must be sealed up while still hot in glass tubes. After exposure to the sun's rays, or to any light rich in ultra-violet rays such as that emitted by burning magnesium wire or the electric arc, it phosphoresces in the dark with a brilliant orange-coloured light. Sulphides of barium, strontium, and calcium are now manufactured for the preparation of luminous paints which are used for coating clock-faces, match-boxes, &c Their surfaces are protected from moisture by a thin coating of varnish. Good Bolognian stones are obtained (J. pr. Chem. ii. 82, 193) from a mixture of strontium carbonate (20 grams), sulphur (3 grams), lithium carbonate (0·5 gram), thorium nitrate (1 c.c. of 0·5 p.c. alcoholic solution), or barium carbonate may be substituted for strontium carbonate and (0·3 gram) rubidium carbonate instead of thorium nitrate. The phosphorescence is more intense if one half of the alkaline earth carbonate is replaced by the corresponding hydroxide. Stones exceeding any others previously made in the intensity and duration of the phosphorescence have been prepared by the ignition for ¾ hour in a Rössler furnace of the following mixture: calcium oxide (10 grams), strontium carbonate (10 grams), barium carbonate (10 grams), magnesium oxide (10 grams), sulphur (6 grams), potassium sulphate (1 gram), sodium sulphate (1 gram), lithium carbonate (2 grams), starch (2 grams), bismuth nitrate (2 c.c. of 0·5 p.c. solution), and thallium sulphate (2 c.c. of 0·5 p.c. solution). The stones exhibit a pale blue phosphorescence. When the ignition is prolonged to two hours the phosphorescence is very intense and greenish-yellow. After three hours' ignition the stones are no longer luminous. The finest green phosphorescence is produced by ignition for ¾ hour of the following mixture: calcium oxide (10 grams), strontium oxide (10 grams), sulphur (3 grams), potassium sulphate (0·5 gram), sodium sulphate (0·5 gram), lithium carbonate (1 gram), starch (1 gram), bismuth nitrate (1 c.c.), rubidium nitrate (1 c.c. 0·5 p.c. solution). Barium sulphide is now largely used in the manufacture of lithophone by adding it dissolved in water to a solution of zinc sulphate. Mutual precipitation takes place, and the white powder formed, consisting of zinc sulphide and barium sulphate, is used as a rubber filler and pigment.

When a solution of 5 parts of barium sulphide is boiled with 1 part of sulphur, and the solution evaporated over sulphuric acid *in vacuo*, colourless six-sided transparent tables of $BaS,6H_2O$ are deposited, which are decomposed by a small quantity of water, forming barium hydrosulphide which dissolves, and barium hydroxide which remains behind.

Barium hydrosulphide $Ba(SH)_2$ is formed by saturating a warm solution of barium hydroxide or sulphide with sulphuretted hydrogen, evaporating apart from the air and cooling, when crystals of baryta and yellow prisms separate out. The mother liquor is mixed with alcohol, filtered from the sulphur and barium thiosulphate formed, and cooled to −10°, when colourless transparent four-sided prisms are obtained. The crystals contain water, which they lose on heating, becoming white. Exposure to air decomposes the crystals, with efflorescence, into barium thiosulphate and sulphate. Heated in a retort, they lose their water of crystallisation without fusing, evolving sulphuretted hydrogen as the temperature approaches redness, and leaving a yellow mass of barium monosulphide, which becomes white on cooling. It is insoluble in alcohol.

Veley (Chem. Soc. Trans. 1886, 369) finds that the composition of crystals of barium sulphydrate is $Ba(SH)_2,4H_2O$.

Barium trisulphide BaS_3 is formed as a greenish-yellow mass when 2 parts of barium sulphide are fused with 1 part of sulphur, the excess of sulphur being distilled off below 360°. It melts at 400° with loss of sulphur and formation of a black liquid. On boiling for some time with water it dissolves to a red liquid which deposits on cooling crystals of the hydrated mono- and tetrasulphides of barium.

Barium tetrasulphide BaS_4. When 7 parts of barium sulphide are boiled in water with 4 parts of sulphur, pale-red rhombic prisms are deposited, soluble in water to a red-coloured liquid from which alcohol precipitates it as an orange-coloured crystalline powder.

Veley (Chem. Soc. Trans 1886, 369) obtains it by dissolving sulphur in a warm saturated solution of barium hydrosulphide; the crystals which separate out have the composition $BaS_4,2H_2O$.

When a mixture of 2 parts of barium hydroxide, 1 part of sulphur, and 25 parts of water is boiled, a deep brown liquid is obtained, which on cooling becomes orange-red in colour. If this solution is evaporated rapidly until a crust is formed on the surface, on cooling the liquid deposits voluminous red prisms of barium tetrasulphide $BaS_4{\cdot}H_2O$ mixed with sulphur and barium thiosulphate. The orange-red liquid contains sulphur and barium in the proportion corresponding with the pentasulphide, which appears to exist in solution, but decomposes during evaporation (Compt. rend. 63, 390).

Barium pentasulphide BaS_5 is obtained in solution by boiling an aqueous solution of the monosulphide with sulphur. On evaporation of the caustic alkaline yellow solution, crystals of barium tetrasulphide and sulphur are obtained: $BaS_5 = BaS_4 + S$.

Barium sulphocarbonate $BaCS_3$ is deposited as a canary-yellow crystalline powder when a solution of barium sulphide is added to carbon disulphide (Thenard, Compt. rend. 79, 673). On the large scale 90 p.c. yield may be obtained, and Dumas suggested its use against the phylloxera in wine districts. Thenard was of opinion that this barium salt would be injurious to the soil, and proposed to convert it into the potassium salt by adding potassium sulphate to its solution.

Barium sulphite $BaSO_3$ is obtained as a white crystalline precipitate by adding potassium or sodium sulphite to a soluble barium salt. Is soluble in a warm solution of sulphurous acid, and crystallises out on cooling in six-sided prisms. When heated in closed vessels it is converted into a mixture of sulphide and sulphate, but heated in air the sulphate is the sole product. Birnbaum and Wittich (Ber. 13, 651) state that BaO unites slowly with SO_2 at 200°, but more rapidly at 230°, forming $BaSO_3$.

Barium sulphate $BaSO_4$ occurs in nature as *barytes*, or heavy-spar, forming fine tabular crystals belonging to the rhombic system. It is a very common mineral in metalliferous veins, and is more particularly associated with lead, silver, and cobalt ores. Clowes (Chem. News, 52, 194) states that the beds of the new red sandstone near Nottingham are permeated by minute crystals of heavy-spar, which acts as a cementing material.

Crystals of artificial barytes, identical in form and properties with native heavy-spar, may be obtained by fusing certain metallic chlorides, such as those of manganese, sodium, potassium, or even barium itself, gradually dissolving barium sulphate in the fused mass, very slowly cooling, and afterwards extracting the soluble chlorides with water. By this means Gorgeu (Compt. rend. 96, 1734) prepared crystals much larger than those obtained by the older process of fusing potassium sulphate with barium chloride. The sp.gr. of the mineral and of the artificial crystals varies from 4·3 to 4·7.

Barium sulphate has been formed by Spring (Bull. Soc. chim. 46, 299) by subjecting an intimate mixture of molecular proportions of sodium sulphate and barium carbonate to great pressure. It is precipitated as a heavy white amorphous powder of sp.gr. 4·0–4·5, when sulphuric acid or a soluble sulphate is added to the solution of a barium salt; this precipitate is nearly insoluble in water (1 pt. in 232,588 pts.), very slightly soluble in dilute acids, more so in strong acids. Concentrated sulphuric acid does not attack anhydrous baryta, but pyrosulphuric acid attacks it so violently that the mass becomes incandescent, and forms barium sulphate. For heat of combinations of Ba and SO_4 ions see Bull. Soc. chim. 1918 (iv.), 23, 13. When freshly precipitated, it is readily soluble in concentrated sulphuric acid at 100°, the solution depositing on cooling lustrous prisms of the *acid barium sulphate* $BaH_2(SO_4)_2$. If the acid solution be exposed to the air, moisture is taken up, and silky needles of a salt having the composition $BaH_2(SO_4)_2$, $2H_2O$ are deposited. Both these acid salts are decomposed by water, yielding sulphuric acid and the neutral salt.

Barium sulphate is also soluble to a perceptible extent in ammonium and potassium nitrates. Hydrobromic acid solution containing 40 p.c. HBr dissolves it to the extent of 1 in 2500 parts acid (Haslam, Chem. News, 53, 87; Karaoglanow. Zeitsch. anal. Chem. 1917, 56, 225).

Barium sulphate is partially decomposed by boiling with a concentrated solution of a fixed alkaline carbonate into alkaline sulphate and barium carbonate, but the reaction is much more complete when the sulphate and alkaline carbonate are fused together. It is reduced to sulphide by ignition with charcoal or organic matter, also by ignition in a stream of coal gas or of hydrogen mixed with vapour of carbon disulphide.

Powdered heavy-spar is used to adulterate white lead, but has not sufficient body to form a pigment by itself; the amorphous sulphate is prepared on the large scale by precipitation of a solution of barium chloride of sp gr. 1·19 by one of sulphuric acid of sp.gr. 1·245, and is used as a pigment under the name of 'permanent white' or 'blanc fixe.'

Barium sodium sulphate $BaNa_2(SO_4)_2$ is formed as an opaque hard mass of pearly lustre by fusing together equivalent quantities of the sulphates of sodium and barium (Berthier).

Barium disulphate BaS_2O_7. If precipitated, barium sulphate be dissolved in fuming sulphuric acid, and the solution heated to 150°, on cooling a glistening deposit of granular crystals of the disulphate is obtained. Decomposition of these crystals occurs at a low red heat without previous fusion.

Barium dithionate $BaS_2O_6,2H_2O$. Prepared by adding barium sulphide to the manganese salt formed on passing sulphur dioxide through finely divided manganese dioxide suspended in water:

$$MnS_2O_6 + BaS = MnS + BaS_2O_6.$$

On allowing the solution to evaporate in a warm place, glittering monoclinic crystals of the salt are deposited of the composition BaS_2O_6,

$2H_2O$. According to Sénarmont and Rammelsberg, the crystals are rhombic. According to V. Lang (Sitz. B. [2] 45, 27), they are monoclinic.

The crystals are soluble in 4 parts of water at 18° and in 1·1 parts at 100°. When the dry salt is heated, it breaks up into sulphur dioxide and barium sulphate. The same decomposition occurs on boiling with hydrochloric acid, but the solution of the dithionate itself in water may be boiled without decomposition.

A tetrahydrate $BaS_2O_6,4H_2O$ may also be obtained by spontaneous evaporation in distinct shining monoclinic crystals, which effloresce on exposure to air.

Barium thiosulphate

$$BaS_2O_3,H_2O \text{ or } BaH_2(SO_2)_2$$

is obtained as a white crystalline precipitate when the sodium salt $Na_2S_2O_3$ is added to barium acetate; it loses its water of crystallisation at 215°. The anhydrous salt, when heated to redness, gives off sulphur and leaves a residue of barium sulphide, sulphite, and sulphate:

$$6BaS_2O_3 = BaS + 2BaSO_3 + 3BaSO_4 + 6S.$$

Barium selenide $BaSe$ is formed by heating barium selenite to redness in a stream of hydrogen. It is decomposed by water into barium hydroxide and a higher selenide, which is decomposed by acids with evolution of H_2Se and precipitation of selenium.

Barium selenate $BaSeO_4$ resembles the sulphate in being insoluble in water, but differs from it in being decomposed by hydrochloric acid into selenite, which dissolves in the hydrochloric acid.

Barium chromate $BaCrO_4$ is precipitated as a yellow crystalline powder when potassium chromate or bichromate is added to the solution of a barium salt. The salt may be obtained in green rhombic crystals isomorphous with $BaSO_4$ by heating two equivalents of $BaCl_2$ with one equivalent of potassium chromate and one of sodium chromate, and allowing the mixture to cool; the chlorides may be boiled out with water, leaving the right rhombic prisms of $BaCrO_4$, of sp.gr. 4·6. They are insoluble in water, but are easily soluble in hydrochloric and nitric acids, and are decomposed by sulphuric acid into $BaSO_4$ and CrO_3 (Bourgeois, Compt. rend. 88, 382).

The precipitated chromate is used as a pigment under the name of 'lemon yellow' or 'yellow ultramarine.' When strong sulphuric acid is added to the dry pigment, great heat is developed, and it is coloured deep red from liberation of CrO_3. If it be now ground in a mortar and heated to bright redness, the chromic acid is reduced to chromic oxide, and a fine green pigment is obtained (Douglas, Chem. News, 40, 59).

Barium dichromate $BaCr_2O_7$ is obtained by dissolving barium chromate in hot concentrated chromic acid. On cooling, red crystals of the composition $BaCr_2O_7,2H_2O$ are deposited, which lose their water at 100°, and are decomposed by water into the normal chromate and chromic anhydride (Preis and Rayman, Ber. 13, 340).

Barium manganate $BaMnO_4$ is formed when manganese dioxide is heated with barium carbonate or nitrate as an emerald-green powder consisting of microscopic four-sided prisms or six-sided plates, insoluble in water but decomposed by acids. This salt is now used in plac of the poisonous Scheele's green.

Barium permanganate $BaMn_2O_8$ is prepared by passing carbonic acid gas through water containing barium manganate in suspension after filtering off the barium carbonate the red solution is rapidly evaporated. Or it may be obtained by the action of barium chloride or silver permanganate.

Or potassium permanganate may be decomposed by slight excess of hydrofluosilicic acid the mixture kept cool, and, after separation o the precipitated potassium silicofluoride, the supernatant solution decanted and saturated in the cold with barium hydroxide. After separation of the insoluble barium silicofluoride, the solution is evaporated until the barium permanganate separates out on cooling (Rousseau and Bruneau Compt. rend. 98, 229).

It forms large orthorhombic octahedra, deep red and almost black, with a violet reflection.

It is used for the preparation of permanganic acid and of the ammonium salt.

Rousseau and Saglier (Compt. rend. 99, 139 find that on heating two grams of barium manganate with ten grams of barium chloride for four hours to 1500°, and extracting with water and dilute acid, a residue of small opaque bluish-black crystals of *barium manganite* $BaMnO_3$ remains; sp.gr. 5·85; readily soluble in hydrochloric acid with evolution of chlorine The manganite is also formed when mixtures o manganese chloride and barium oxychloride are heated below 1000° or above 1100°. Between these temperatures the product is barium dimanganite $BaO{\cdot}2MnO_2$, which crystallises in brilliant black lamellæ. At 1500° the manganite is reconverted to manganate.

Barium phosphide Ba_3P_2. When vapour o phosphorus is passed over red-hot baryta, a brownish-red mixture of barium phosphide and phosphate is obtained commonly known as 'phosphuret of baryta.' It is decomposed by water, forming a solution of hypophosphite o barium and evolving a mixture of free hydrogen and spontaneously inflammable phosphoretted hydrogen.

Jaboin (Compt. rend. 129, 762) prepared the phosphide by heating 100 parts of barium phosphate with 16 parts of lamp black in an electric furnace. The product so obtained has a crystalline structure. It decomposes water yielding PH_3 and $Ba(OH)_2$.

Barium monometaphosphate is obtained as a white powder by evaporating a solution o barium carbonate in excess of metaphosphoric acid and heating the residue to 316°. Its formula is not known with certainty.

Barium dimetaphosphate $Ba(PO_3)_2,2H_2O$ is formed as a crystalline sparingly soluble precipitate when barium chloride is added to a solution of the corresponding ammonium or sodium salt

Barium trimetaphosphate $Ba_3P_6O_{18},6H_2O$ apparently a polymeric form of the last salt, is produced when a solution of 1 part of the corresponding sodium salt in 10 to 15 parts of water is mixed with a nearly saturated solution o 3 parts barium chloride. On standing, the salt separates in monoclinic prisms, which give off two-thirds of their water at 100°, and the rest at a higher temperature.

Barium hexametaphosphate is obtained as a gelatinous precipitate by precipitating the corresponding sodium salt with barium chloride.

Monobarium orthophosphate $BaH_4(PO_4)_2$ is prepared by evaporating a solution of the di- or tri-barium salt in aqueous phosphoric acid. It forms colourless crystals—triclinic according to Erlenmeyer, with acid reaction; soluble without decomposition in a small quantity of water, but decomposed by excess of water into free phosphoric acid and the neutral salt.

Joly (Compt. rend. 98, 1274) states that as the total weight of salt brought in contact with the same quantity of water increases in arithmetical progression, the weight which is dissolved without decomposition decreases in geometrical progression; but as soon as half the original salt has been decomposed a diacid salt is formed $BaO{\cdot}2P_2O_5+xH_2O$, the proportion of which increases as the acidity of the liquid increases, and eventually exists alone in solution.

Dibarium orthophosphate $Ba_2H_2(PO_4)_2$ or $BaHPO_4$ is obtained as a white, scaly, crystalline precipitate when hydrogen disodium phosphate is added to a neutral solution of a barium salt. It is soluble in 20,570 parts of water at 20°, somewhat more soluble in water containing barium or sodium chloride or ammoniacal salts. From the solution in nitric or hydrochloric acid excess of ammonia precipitates the tribarium salt or a salt intermediate between the two. Thus, according to Wackenroder, a solution of $BaHPO_4$ in nitric acid yields, on addition of ammonia, a precipitate of barium phosphato-nitrate $4BaHPO_4{\cdot}Ba(NO_3)_2$, which leaves, on heating, a mixture of di- and tri-barium phosphates.

By precipitating a solution of dibarium phosphate with alcohol, a salt intermediate between the mono- and di-salts is obtained:

$$BaH_4(PO_4)_2{\cdot}2BaHPO_4,3H_2O.$$

If a mixture of potassium silicate and baryta water is boiled, and afterwards mixed with a solution of potassium silicate containing a quantity of potassium phosphate, on cooling, cubical crystals of the composition $BaKPO_4,10H_2O$ separate out. $BaNaPO_4,10H_2O$ was similarly obtained in regular tetrahedrons (De Schulten, Compt. rend. 96, 706).

Tribarium orthophosphate, or neutral phosphate of barium, $Ba_3(PO_4)_2{\cdot}H_2O$ is prepared by adding hydrogen disodium phosphate to a solution of barium chloride rendered strongly alkaline by ammonia, and separates as a heavy granular powder. It parts with a portion only of its water at 200°.

If a saturated solution of tribarium phosphate in hydrochloric acid is evaporated, on cooling, crystals of barium chloride are deposited, more and more monobarium phosphate being left in solution, and if more hydrochloric acid is added, all the barium may be crystallised out as barium chloride, and pure phosphoric acid remains.

If the solution of tribarium phosphate in hydrochloric acid is boiled, shining needles form in the liquid, and on adding sufficient water to redissolve them, well-defined crystals of a phosphato-chloride $4BaH_4(PO_4)_2{\cdot}BaCl_2$ are deposited on standing (Erlenmeyer, J. 1857, 147).

According to Ludwig, a solution of dibarium phosphate in hydrochloric acid also yields, on addition of ammonia, a phosphato-chloride containing $3Ba_5H_2P_4O_{16}{\cdot}BaCl_2{\cdot}3H_2O$.

A salt intermediate between the di- and tri-phosphates, containing $Ba_3(PO_4)_2{\cdot}2BaHPO_4$ or $Ba_5H_2P_4O_{16}$, is formed when a solution of the dibarium phosphate in hydrochloric acid is mixed with a quantity of ammonia just sufficient to precipitate it.

Barium pyrophosphate $Ba_2P_2O_7$. Pyrophosphoric acid does not precipitate barium salts, but with baryta water gives a precipitate of barium pyrophosphate. Barium salts, however, give with sodium pyrophosphate a white amorphous precipitate of barium pyrophosphate, soluble in aqueous pyrophosphoric and sulphurous acids; more soluble in hydrochloric or nitric acid, but not perceptibly soluble in water containing ammonium chloride or in acetic acid.

Monobarium arsenate $BaH_4(AsO_4)_2$ is obtained by adding baryta water to aqueous arsenic acid until a precipitate begins to form, or by dissolving the dibarium salt in aqueous arsenic acid and leaving the solution to crystallise.

Dibarium arsenate

$$2BaHAsO_4,H_2O \text{ or } BaHAsO_4,H_2O$$

according to Berzelius, is obtained when a solution of the disodium salt is added to excess of barium chloride. It gives up its water at a red heat, and in contact with water is decomposed into the tribarium salt, which is precipitated, and the monobarium salt, which dissolves.

Tribarium arsenate $Ba_3(AsO_4)_2$ is obtained as a white sparingly soluble powder by precipitating aqueous arsenic acid with baryta water, or better, by gradually dropping trisodium arsenate into barium chloride.

Barium ortho-thioarsenate $Ba_3(AsS_4)_2$ is obtained together with $Ba(AsS_3)_2$ by the action of hydrogen sulphide on a solution of $BaHAsO_4$. The barium thioarsenate is precipitated by adding alcohol. Arsenic pentasulphide prepared by the action of a rapid stream of hydrogen sulphide on a solution of arsenic acid and hydrochloric acid, reacts with a freshly prepared solution of $Ba(SH)_2$ according to the equation

$$3Ba(SH)_2+As_2S_5=Ba_3As_2S_8+3H_2S$$

After evaporation transparent yellow needles of $Ba_3As_2S_8,6H_2O$ separate (Zeitsch. anorg. Chem 70, 86). A solution reacts with potassium chloride yielding potassium barium ortho-thioarsenate $BaKAsS_4,6H_2O$, which may also be prepared direct by adding KCl to a solution of $Ba(SH)_2$ saturated with As_2S_5.

Barium silicate. Solutions of baryta, when kept in glass bottles for any length of time, deposit transparent rhombic crystals of the composition $BaSiO_3,7H_2O$. These crystals lose their water a little above 100°, and become turquoise-blue: they are decomposed by boiling water (Le Chatelier, Compt. rend. 92, 931); Cossa and Lavalle (Zeitsch. f. Chem. 11, 399).

According to Le Chatelier, they may be readily obtained in a few days, by suspending calcined silica in baryta water, when the sides become covered with crystals.

Barium disilicate $BaSi_2O_5$ has been prepared synthetically. It crystallises in the orthorhombic system. The colourless six-sided plates which form in optical glass rich in barium have been identified with this compound.

Barium titanate. When equivalent quantities of titanic anhydride and barium carbonate are fused at a bright red heat for an hour with excess of barium chloride, and the product extracted with very dilute hydrochloric acid, a residue of yellow microscopic crystals resembling cubes and octahedra of the composition

$$2BaO\ 3TIO_2$$

and of sp.gr. 5·91 remains undissolved. These crystals are found on examination by polarised light to consist of aggregations of rhombic lamellæ.

Reactions of the compounds of barium. When heated on a thin platinum wire in the inner blowpipe flame, or when brought into any non-luminous flame, barium compounds impart a yellowish-green colour to the outer flame. When viewed through the spectroscope two green lines Baα and Baβ come out most intensely; Baγ, though not so marked, is also a characteristic line. Besides these, there are numerous lines in the red and yellow and one broad indistinct line in the blue, close to Fraunhofer's F. Bunsen found that $\frac{1}{1000}$ of a milligram of barium salt may be detected spectroscopically. Silicates of barium give this reaction on moistening with strong hydrochloric acid.

The hydrate, sulphide, chloride, bromide, iodide, nitrate, and many organic salts of barium are soluble in water, and all are poisonous. The majority of the remaining salts are soluble in hydrochloric and nitric acids, whilst the sulphate and silicofluoride are insoluble in all acids.

Alkaline carbonates precipitate white barium carbonate, soluble in most acids, hence ammonium carbonate is used to precipitate it (along with the carbonates of strontium and calcium) in qualitative analysis.

Potassium and sodium hydroxides, free from carbonates and sulphates, give a voluminous precipitate of barium hydroxide $Ba(OH)_2$ with concentrated solutions soluble in more water. Ammonia gives no precipitate.

Sulphuric acid, as well as all soluble sulphates, throws down barium sulphate from all solutions of barium salts. Pickering (Chem. News, 40, 223) states that the smallest quantity of barium which can be detected is 1 part in 833,000 parts of water. The presence of an alkaline citrate greatly interferes with the precipitation. Strontium sulphate (which is more soluble) forms a delicate test for barium.

Phosphate, arsenate, borate, and iodate of sodium also give precipitates soluble in acids.

Ammonium oxalate gives, from moderately dilute solutions, a white pulverulent precipitate of barium oxalate.

Potassium chromate precipitates bright lemon-yellow barium chromate, soluble in nitric, hydrochloric or chromic acid, insoluble in dilute acetic acid.

Hydrofluosilicic acid gives a colourless crystalline precipitate of barium silicofluoride; this reaction will detect 1 part of the chloride in 3800 parts water. The precipitate is nearly insoluble in nitric and hydrochloric acids, more insoluble in alcohol.

Barium is readily distinguished from lead (which also forms a sulphate insoluble in water) by the fact that sulphuretted hydrogen gives a black precipitate of lead sulphide with soluble lead salts.

Soluble barium salts are at once distinguished from those of strontium and calcium by the fact that they are immediately precipitated by a solution of calcium sulphate, which only gives a precipitate with strontium salts on standing. The hydrofluosilicic acid reaction is also of use in separating barium from the other two metals. Barium chloride is insoluble in alcohol, whilst the chlorides of strontium and calcium are soluble, and the nitrates of barium and strontium are insoluble, in alcohol, whilst calcium nitrate is soluble. From these facts a scheme of separation is readily derived, the precipitated carbonates of barium, strontium, and calcium being converted into chlorides, and the chlorides of strontium and calcium dissolved out by alcohol, leaving a residue of chloride of barium. The strontium and calcium may then be separated by converting their reprecipitated carbonates to nitrates and dissolving out the calcium nitrate (*v.* ANALYSIS).

Estimation of barium. When no other alkaline metal is present, barium may be estimated as sulphate. A solution of the chlorides slightly acidified with hydrochloric acid is best. Sulphuric acid is added cautiously to the hot solution in slight excess. The precipitate is allowed to settle in a warm place for some hours before filtering.

For precautions and effect of salts, see work of Karooglanow (Zeitsch. anal. Chem. or Abstrs. J. Chem. Soc. for 1917). For details of volumetric estimation of barium by separation as chromate and titration of liberated iodine, on addition of KI to HCl solution, see Analyst, 43, 287.

In its organic salts barium may be estimated as carbonate by heating in a platinum crucible and subsequent moistening of the residue with a concentrated solution of ammonium carbonate, evaporation, gentle ignition, and weighing.

Where strontium and calcium are present, after the separation of the other elements, the alkaline earths are precipitated by ammonia and ammonium carbonate. This precipitate is then dissolved in acetic acid, and the barium twice precipitated as chromate, in which form it may be weighed or dissolved in hydrochloric acid, then precipitated, and weighed as sulphate.

G. S. B.

BARK BREAD. A kind of bread which was formerly made by the peasants in various parts of Norway from the inner bark of *Pinus sylvestris* (Linn.).

BARKLYITE *v.* CORUNDUM.

BARLEY. Two species are in common cultivation—*Hordeum distichum*, two-rowed, and *H. vulgare*, six-rowed. Many varieties are known, differing in size and shape of ear and grain. The two-rowed varieties are chiefly grown as spring-sown crops, while the six-rowed varieties are often sown in the autumn.

The grain resembles in composition that of other cereals, but contains less gluten than wheat; moreover, the gluten of barley is not so tenacious as that of wheat: consequently, barley meal does not yield a satisfactory bread.

Barley is chiefly grown for cattle-feeding and for malt production. For the latter purpose, a grain containing but little nitrogenous matter is preferred, so that too lavish nitrogenous manuring must be avoided in the production of malting barley.

The following are analyses of typical average barley as given by 1, Warington; 2–5, Kellner (German); 6, Wiley (of American barley).

The table represents the composition of barley expressed in the usual manner. The item 'nitrogenous substances' is simply the total nitrogen ×6·25. Of the total nitrogen, a small portion—probably about $\frac{1}{100}$—is present in non-albuminoid form.

	1 English	2 Medium	3 Large gr'nd	4 Flat gr'nd	5 Feeding	6 American
Water . .	14·3	14·3	14·3	14·3	14·3	10·85
Nitrogenous substances	10·6 [1]	9·4	8·7	10·2	12·0	11·00
Fat . . .	2·1	2·1	1·8	2·5	2·4	2·25
Soluble carbohydrates .	66·0	67·8	70·2	63·7	63 7	69·55
Fibre . . .	4·5	3·9	2·7	6·5	5·0	3·85
Ash . . .	2·5	2·5	2·3	2·8	2·6	2·50

According to Osborne (18th Ann. Rep. Conn. Expt. St.), the proteids in barley are: (1) Soluble: leucosine 0·30 p.c., hordein 4·0 p.c., edestine and proteose 1·95 p.c.; (2) insoluble proteids 4·50 p.c. The soluble proteids just mentioned contain an average of 17·6 p.c. of nitrogen, so that the factor to convert nitrogen into proteids in barley should be much less than 6·25, probably about 5·7. Consequently, the amount of proteids in barley should be about 1 p.c. less and that of carbohydrates (since they are determined by difference) 1 p.c. more than the values given in the tables.

Under the heading 'soluble carbohydrates' are included: pentosans 6·5 p.c. (Bull. 13, U.S. Dept. of Agric. 1898); cane sugar 0·8–1·6 p.c. (O'Sullivan, J. Chem. Soc. 1886, 49, 58); 1·3 p.c. (Banister, Chem. News, 1885, 298); 0·2 p.c. (Bull. 13, *l.c.*); small quantities of reducing sugars (O'Sullivan); dextrine and raffinose (O'Sullivan). The remainder is chiefly made up of starch and cellulose, though gum 2·8 p.c. (Muntz, Compt. rend. 102, 681) and amylan 2–4 p.c. (O'Sullivan, J. Chem. Soc. 41, 24) have also been found.

Barley contains diastase even before germination (when its amount is enormously increased). Brown and Morris (J. Chem. Soc. 1890, 505) recognise two kinds of diastase—of secretion, as formed in germination, which rapidly corrodes starch granules, and of displacement—present in the ungerminated grain - which slowly diminishes the volume of starch granules without visibly corroding them.

The ash of barley, neglecting the CO_2, has the average composition:

—	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	Cl	SiO_2
[2] Mean, 28 American samples	24·15	6·42	2·44	8·23	0·33	35·47	0 22	0·56	22·30
[2] „ 19 Canadian „	26·76	9·36	4·27	7·87	0·35	24·63	0·71	0·47	20·69
„ Wolff's analyses .	20·15	2·35	2·60	8 62	0·97	34·68	1·69	0·93	27·54

For a full yield of barley the soil must be well supplied with plant food, including combined nitrogen, but such a crop, though excellent from the farmer's point of view and valuable for feeding purposes, is rarely suited to the maltster's requirement. Good malting barley should be as rich as possible in starch and low in albuminoids. Between 8 and 9 p.c. of nitrogenous matter is usually regarded as the most desirable proportion in malting barley. If grown in hot, dry countries, *e.g.* Southern Russia, it is usually richer in nitrogen. The best malting barleys are grown on light soils not too rich in nitrogen, and in temperate climates (*v.* BREWING).

Owing to the injurious effect of too lavish a supply of nitrogen upon the malting properties of barley, it is by many considered best to take the barley crop after wheat, rather than after roots, though the latter procedure is often adopted in Ireland.

Pearl barley is barley deprived of its husk. American analyses give as its average composition: Water, 10·8 p.c.; protein, 9·3 p.c.; fat, 1·0 p.c.; carbohydrates, 77·6 p.c.; ash, 1·3 p.c.

According to Wolff's analyses, the ash of the barley kernel amounts to 2·13 p.c., and 100 parts of the ash contain:

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2
28·5	1·8	3·1	12·0	1·9	47·1	2·9	3·6

Barley straw is much more affected in composition than the grain by the richness or poverty of the soil, and by the conditions under which it is grown. If the ripening of the grain has been fully completed, the straw is robbed of its nitrogenous matter and phosphates to a much greater extent than when the seed has not been fully matured. Thus the straw of a crop cut before it is fully ripe possesses much higher feeding value than usual.

According to Kellner, the following represents the average composition of barley straw:—

	Water	Protein	Ether extract	Soluble carbohydrates	Fibre	Ash
Summer barley	14·3	3·5	1·4	35·9	39·5	5·4
Winter barley	14·3	3·2	1·4	33·5	42·0	5·6

The ash of barley straw (Wolff) contains:

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
23·3	3·5	7·2	2·6	1·1	4·2	3·9	51·0	3·2

Barley straw consists largely of cellulose, and pentosans and lignose. The amount of pentosans has been estimated at about 25 p.c. The 'crude protein' given in the above table is probably nearly all true albuminoids, since direct experiments showed about 91 p.c. of the total nitrogen to be present as albuminoids. The lowest portions of the stems are least nutritious, while the uppermost leaves and top of the stem are the most digestible and richest in protein.

When barley precedes clover, as is often the case in England, the barley straw is enriched by including a portion of young clover plants. Under such circumstances, the product is of much higher feeding value, and contains more protein (up to 6 or 7 p.c.), and soluble carbohydrates (38 or 39 p.c.), and less crude fibre.

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[1] Of which 10·2 p.c. are albuminoids.

[2] Composite samples from the World's Columbian Exposition (Wiley, Bull. 13, U.S. Dept. of Agric.).

H. I.

BARRESWIL'S or FEHLING'S SOLUTION. It has long been known that a mixture of verdigris, honey, and vinegar, when boiled together to form an ointment, changes in colour from green to red.

Vogel (Schweigger's Journ. 13, 162) proved that the precipitate formed consisted of cuprous oxide, and later Buchner attempted to explain the part played by the sugar in the change. Trommer first used alkaline copper sulphate solution as a qualitative reagent for sugars, and succeeded in detecting one part of grape sugar in a million parts of water, and also in differentiating between different kinds of sugars (Annalen, 1841, 39, 360).

Alkaline copper solution was first applied to volumetric analysis by Barreswil (J. Pharm. Chim. 1844, [3] 6, 301), who added potassium tartrate to the solution, and the method of titration was worked out by H. Fehling (Annalen, 1849, 72, 106; 1858, 106, 75).

Various formulæ have been suggested for the preparation of Barreswil's solution by Bödekerr, Soxhlet, Meissl, Herzfeld, Allihn, Kjeldahl, &c. (Bruhns, Zeitsch. anal. Chem. 1899, 38, 78). Indeed, more than fifty cupropotassic solutions are known. They may be divided into four groups, in which potassium hydrogen tartrate, (2) potassium sodium tartrate, (3) potassium tartrate, and (4) tartaric acid are employed. That recommended by Soxhlet is usually preferred, partly on account of its small alkali content.

34·64 grams of pure crystallised copper sulphate, powdered and dried by pressure between filter paper, is dissolved in distilled water and diluted to 500 c.c.; and 70 grams sodium hydroxide (of not less than 97 p.c.) and 180 grams of potassium sodium tartrate (Rochelle salt) are dissolved in 400 c.c. of distilled water and diluted to 500 c.c. Equal volumes of the two solutions are mixed to form the test, which should be kept in a carefully closed bottle to prevent absorption of carbon dioxide, and should not be unduly exposed to light. As the solution is liable to decomposition, a small portion should always be heated to boiling before commencing the test, and the liquid should not be used if any precipitation occurs. It is, however, preferable to keep the two solutions separate until shortly before use (Zeitsch. anal. Chem. 1890, 29, 615).

The Rochelle salt used is best prepared by dissolving commercial cream of tartar in hot water, rendering the liquid slightly alkaline after boiling by addition of sodium carbonate, filtering off the precipitated calcium carbonate, and crystallising the Rochelle salt from the filtrate.

Addition of small quantities of mineral acids to Barreswil's solution by lessening its alkalinity effects its reduction, even when it is still alkaline to litmus. Often the action commences before the liquid is warmed, reduction being completed by gentle heating. The reduction is attributed to the decomposing action of the mineral acid upon the tartaric acid (Jovitschitsch. Ber. 1897, 2431). Evidence of the negative character of the blue ion in Barreswil's solution was first adduced by Kahlenberg (Zeitsch. physikal Chem. 1895, 17, 586), and later by Küster (Zeitsch. Elektrochem. 1897, 105) and Masson (Phil. Trans. 1899, 192, 331).

Masson employed a solution as free as possible from alkali, and electrolysed it in conjunction with a solution of copper sulphate, the blue ions in the two solutions travelling in opposite directions along a tube containing a jelly solution of potassium chloride. The presence of an invisible ion, probably tartaric ion, accompanying the negative blue ions, was demonstrated by the formation of a precipitate at the boundary of the positive blue ions, when the negative ions were still some way off.

The constituent salt of the neutral Barreswil's solution was isolated and analysed by Masson and Steele (Chem. Soc. Trans. 1899, 75, 725), who represented its formation from cupric tartrate thus:

$$5NaOH+4CuC_4H_4O_6$$
$$=Na_2C_4H_4O_6+Na_3C_{12}H_7Cu_4O_{18}+5H_2O$$

They also obtained evidence that the excess of alkali in Barreswil's solution, as usually made, is combined with the blue salt.

F. Bulluheimer and E. Seitz (Ber. 1899, 2347; 1900, 817) showed that three classes of cupric tartrates exist; monotartrates, containing carboxylic and hydroxylic hydrogen, all replaced by metal; double salts consisting of monotartrate, probably united through copper to a molecule of basic alkali tartrates; and a third class consisting of monotartrate combined with basic cupric tartrate.

The salts in Barreswil's solution, from their general reactions, appear to belong to the second class, and compounds having the formulæ $C_8H_4O_{12}CuNa_2K_2$ and $C_8H_4O_{12}CuNa_3K$ have been isolated.

The neutral cuprotartrate of Masson (*l.c.*) requires the addition of alkali in order to form the usual Barreswil's solution with its characteristic colour.

Barreswil's solution is *not reduced* by cane sugar, dextrin, or cellulose, but *is reduced* by dextrose, lævulose, maltose, lactose, mannose, galactose, arabinose, gallisin, aldehyde, chloral, chloroform, valeraldehyde, resorcinol, pyrogallol, gallotannic and trichloracetic acids, and by arsenious acid.

The action of these substances on the solution is doubtful. Among the products are formic, acetic, tartronic, and some acids of doubtful composition and a gum-like substance. Its use is almost restricted to the detection and estimation of reducing sugars. For the *detection* of sugars, the clear, acid-free liquid is heated with two volumes of Barreswil's solution. If one of the above reducing compounds be present, a yellow precipitate of cuprous oxide, which rapidly becomes converted into the orange-red or bright red oxide, is produced. The composition of the oxide whatever its colour may be is identical, the varying colour being due to differences of subdivision, depending upon the conditions during precipitation. Microscopical examination shows that as the different colours are developed there is a gradual increase in the size of the particles (Fischer and Hooker, J. Lab. and Clin. Med. 1918, 3, 6).

If the liquid to be tested is much coloured, it must be first clarified, as described under **Saccharimetry**. When the clarification has been performed with lead, an amount of the solution containing a known weight (2 to 5 grams) of glucose or other body, estimated, is placed in a 100 c.c. flask and is treated with sulphurous acid gas, or with a strong solution of that gas, until the whole of the lead is precipitated, and, after the addition of a little freshly precipitated, washed alumina, is diluted to 100 c.c., agitated and filtered.

Cane sugar, when estimated, is first clarified, if necessary, and then 'inverted'—*i.e.* converted into a mixture of dextrose and lævulose. For this purpose, a solution containing not more than 1 gram of sugar to 4 c.c. of solution is mixed with one-tenth its bulk of fuming hydrochloric acid, and is heated to 70° for 10 to 15 minutes, and finally neutralised by addition of sodium carbonate.

Starch and starchy bodies may also be converted into invert sugar, and estimated by Barreswil's solution. Two or three strong flasks, each containing from one-half to one gram of the substance and 50 or 60 c.c. of decinormal sulphuric acid solution, are closed with caoutchouc corks carefully tied down, and are heated in a water-bath. After 4 hours, one flask is taken out and contents neutralised and titrated with Barreswil's solution as hereafter described, and after a further interval of 2 hours the second is similarly examined. If the amount of sugar found in the second flask does not exceed that in the first, the result may be taken as correct; but if the quantities differ markedly, the third flask is heated a further period of from 2 to 4 hours, and then titrated. Each 100 parts of invert sugar found represents 90 parts of starch.

In titrating solutions of these substances, 10 c.c. of Barreswil's solution is measured into a wide test-tube and diluted to 40 c.c., and heated to boiling. The neutralised sugar solution, which should contain not more than one gram per 100 c.c., is then run in from a burette in portions of 2 c.c., the mixture being boiled after each addition until the blue colour has nearly disappeared. The sugar is then added cautiously until the liquid is colourless or slightly yellow. A few drops of the filtered solution are tested for copper by sulphuretted hydrogen or by a mixture of potassium ferrocyanide and acetic acid.

The solution may be standardised for invert sugar as follows: 4·75 grams of sucrose are dissolved in 75 c.c. water, and 5 c.c. of hydrochloric acid (sp.gr. 1·188) added. The solution is warmed to 70° for about 7 minutes, making a total of 10 minutes' heating. After inversion, the acid is neutralised with sodium hydroxide, and the liquid diluted to 1 litre. 10 c.c. of this solution contains 0·050 gram of invert sugar, and should reduce 10 c.c. of the copper solution (*see also* Börntrager, Zeitsch. angew. Chem. 1893, 600).

Experience shows that the time occupied in the analysis, the amount of excess of copper present in the solution, the concentration of the liquid, and other details, affect the result. Soxhlet (Pharm. J. [3] 1880–1, 11, 721) recommends adherence to the following process. Having approximately found the strength of the solution by running the sugar solution into 50 c.c. of Barreswil's solution as above until the blue colour disappears, dilute it until containing about 1 gram per 100 c.c., and heat 50 c.c. Barreswil's solution with as much of the diluted solution as should precipitate all the copper. When the sugar estimated is invert sugar, grape sugar, or lævulose, the heating should occupy 2 minutes, while for maltose and lactose 4 and 6 minutes respectively should be allowed. The whole fluid is then filtered and tested for copper. A third titration is next performed with a larger amount of the fluid, with 1 c.c. less of sugar (according to the presence or absence of copper), and the titrations are repeated with varying amounts of sugar solution, each time adding the whole of that solution at once, until 1 c.c. more or less would give a filtrate free from or containing a trace of copper, after which the variation in the amount of sugar solution is decreased. In this way, the volume of sugar solution required may be determined to 0·1 c.c. Under these conditions, 100 c.c. of the mixed copper reagent require 0·475 gram anhydrous dextrose or 0·494 gram of invert sugar for complete reduction. The following may be taken as the weight of sugar capable of reducing 10 c.c. of Barreswil's solution:—

	gram
Dextrose, lævulose, or invert sugar	0·0500
Cane sugar (inverted) . . .	0·0475
Milk sugar (lactose) . . .	0·0678
Malt sugar (maltose) . . .	0·0807

Soxhlet (*l.c.*), operating by his method as described above, has obtained the following results. (His method of 'inverting' cane sugar has been somewhat objected to)—

WEIGHT OF SUGAR REDUCING 10 C.C. OF BARRESWIL'S SOLUTION.

—	Time of heating (mins.)	Un-diluted	Diluted with			
			One vol. of water	Two vols. of water	Three vols. of water	Four vols. of water
Dextrose	2	0·0475	0·04825	0·0488	0·0492	0·0494
Invert sugar	2	0·0494	0·05030	0·0509	0·0514	0·0515
Lævulose	2	0·0513	0·05235	0·0530	0·0536	0·0526
Lactose	6	0·0676	Unaffected by dilution			0·0676
Lacto-glucose	2	0·0511	„		„	0·0538
Maltose	3 to 4	0·0778	„		„	0·0740

The titration of raw sugars and other coloured commercial products is very unsatisfactory when potassium ferrocyanide is used as an indicator, mainly because the amino compounds present cause the solution of much cuprous oxide, which then gives a precipitate with potassium ferrocyanide. On this account, indicators have been proposed which will show the presence of a trace of cupric salt without previous filtration, the best of these being ferrous thiocyanate (A. R. Ling, T. Rendle, and G. C. Jones, Analyst, 1905, 30, 182; 1908, 33, 160–170), which gives the characteristic red colour of ferric thiocyanate when treated with cupric salt solution. The reagent is prepared by dissolving 1 gram of ferrous ammonium sulphate and 1·5 grams of ammonium thiocyanate in 10 c.c. of warm water, adding 2·5 c.c. of conc. hydrochloric acid, and completely removing all trace of ferric salt by addition of zinc-

dust. The titration of the sugar solution is carried out much as usual, except that it must be done as quickly as possible to avoid oxidation (Ling. J. Inst. Brewing, 1906, 12, No. 1).

A modification of Barreswil's process, devised by Pavy, is based on the fact that precipitation of the cuprous oxide is prevented by the presence of excess of ammonia, the solution losing its intense blue colour and becoming absolutely colourless after the whole of the copper has been reduced.

The solution used is prepared by mixing 120 c.c. of Barreswil's solution with 300 c.c. of ammonia (0·880 sp.gr.) and 400 c.c. of 12 p.c. caustic soda solution, and diluting to 1 litre. 100 c.c. of this solution corresponds with 10 c.c. of Barreswil's solution. The larger quantity of Barreswil's solution (120 c.c. instead of 100 c.c.) used to prepare this test is required on account of the lower oxidising power of Pavy's solution, the action of which on invert sugar is only five-sixths of that of Barreswil's solution. Its action on maltose and lactose also differs from that of Barreswil's solution.

To prevent reoxidation of the decolourised solution, with reproduction of the blue colour, the operation should be performed without access of air, by connecting the burette supplying the sugar solution with a tube passing through a cork into the flask containing the Barreswil's solution, the steam from which escapes through another tube dipping beneath the surface of mercury. A slow current of coal gas may be passed through the flask during the operation.

The sugar solution is run into the flask, in which 100 c.c. of the copper solution has been heated to ebullition, and the boiling is continued until the colour has disappeared. Hehner (Analyst, 1881, 6, 218) has shown that alkaline tartrates, carbonates, and other salts affect the results.

The method is most used in clinical chemistry, particularly for urine analysis. It is also of great value in studying the saccharine products of enzyme action, especially as it gives with glucose a very much larger 'copper' value than with maltose (Croft Hill, Chem. Soc. Trans. 1898, 73, 634).

The most accurate method of using Barreswil's solution, especially when the sugar solution is unclarified, consists in separating and estimating the precipitated cuprous oxide One of the many processes recommended is that of Pavy. The Barreswil's solution is boiled, in slight excess, with the sugar solution, the strength of which should be about 1 p.c., and the precipitated suboxide is rapidly separated by filtering the liquid through a funnel loosely packed at the neck with glass wool or asbestos. The precipitate, after washing, is dissolved in hot dilute nitric acid, or 2 p.c. conc. nitric acid, or a mixture of dilute sulphuric and nitric acids, and the copper estimated by electro-deposition. The weight of copper obtained is multiplied by 0·5395 to obtain its equivalent in inverted cane sugar, or by other factors, which may be calculated from the tables given above, to obtain the equivalent of any other sugar which may be estimated.

Brunner recommends solution of the cuprous oxide, filtered as above, in a solution of pure ferric chloride or sulphate acidulated with sulphuric acid, and the estimation of the ferrous salt so produced, by titration with a standard solution of potassium permanganate or dichromate.

The cuprous oxide can also be weighed directly after washing with alcohol and ether. It may also be estimated as metallic copper after reduction by hydrogen or as cupric oxide after ignition in porcelain.

For the influence of light on Barreswil's solution, *see* Leighton (J. Phys. Chem. 1913, 17, 205).

BARUS CAMPHOR *v.* CAMPHORS.

BARUTIN. Trade name for the double salt of theobromine barium and sodium salicylate; a white amorphous powder of sweetish taste and alkaline reaction, sparingly soluble in water. Used in the treatment of renal disease. *V.* SYNTHETIC DRUGS.

BARWOOD. Barwood is the wood of a large, fine tree, *Baphia nitida* (Lodd.), and is imported from the west coast of Africa, *e.g.* Sierra Leone, Angola, &c. In the log its physical properties are generally similar to those of sanderswood; in the rasped condition it has a somewhat brighter red colour and is devoid of aromatic odour. According to Girardin and Preisser, boiling water extracts about 7 p.c. of colouring matter, alcohol about 23 p.c., and hydrated ether about 10 p.c.

Anderson (Chem. Soc. Trans. 1876, ii. 582) extracted ground barwood with anhydrous methylated ether free from alcohol. By spontaneous evaporation of the concentrated ethereal solution a small quantity of *baphic acid* is deposited in the form of tabular crystals. After further evaporation, mixing the concentrated extract with alcohol, and allowing to stand for some days, there is deposited a crystalline magma of *baphiin* contaminated with a solid red colouring matter and some dark viscous colouring matter not yet examined.

After exhaustion with ether the wood is extracted with alcohol, and after concentrating the solution it is left at rest for some time, when it congeals to a semi-crystalline mass which contains a viscous red colouring matter and a crystalline constituent not examined.

Baphiin, $C_{24}H_{20}O_8$ (m.p. about 200°), crystallises from alcohol in the form of lustrous tabular crystals having an odour of orris root; from ether it crystallises in tufts of needles. It is insoluble in water, and very sparingly soluble in benzene or in carbon disulphide. In alcoholic solution it rapidly oxidises on exposure to air, producing orange-red or pale purple colours.

Baphic acid $C_{24}H_{22}O_9$ or $C_{24}H_{22}O_{10}$ is prepared by boiling baphiin with dilute caustic potash, and adding hydrochloric acid, when it is thrown down as a yellowish-white precipitate. Crystallised from ether it forms white nacreous scales, very soluble in ether, slightly less so in alcohol, and insoluble in water (*cf.* Santal).

Baphinitin $C_{24}H_{24}O_6$ is thrown down as a crystalline precipitate on the addition of water to the filtrate from the precipitate of lead baphate which is formed on mixing alcoholic solutions of baphiin and lead acetate. It is also the chief product of the action of boiling dilute caustic potash on baphiin. Baphinitin forms white needles, soluble in alcohol or in ether, but insoluble in water; it has the same odour as baphiin but stronger (*cf.* Pterocarpin).

Baphinitone $C_{26}H_{26}O_6$.—On boiling baphiin with a strong aqueous solution of caustic potash without access of air, an insoluble residue is left which contains three substances: (1) baphinitin, moderately soluble in alcohol or ether; (2) baphinitone, very readily soluble in these liquids; (3) a small quantity of an unexamined substance, m.p. 164·1°, very sparingly soluble even in hot alcohol, and separating therefrom in granular crystals. Baphinitone is extracted from the above-mentioned residue insoluble in caustic potash, by treating it with cold alcohol, in which it readily dissolves along with a very small amount of baphinitin. The solution is evaporated, and the treatment with alcohol is repeated until the crystals thus obtained, after drying over sulphuric acid, have a m.p. of about 88°. Baphinitone crystallises from alcohol in hemispherical masses composed of white lustrous radiating crystals insoluble in water (*cf.* Homopterocarpin).

Tribromo-baphinitone $C_{26}H_{23}Br_3O_6$ is obtained by mixing ethereal solutions of baphinitone and bromine; on evaporating off the ether it remains as a white substance, which may be purified by washing with alcohol or ether, in which it is almost insoluble. It separates from a hot ethereal solution in small granules, which melt with blackening at 180·2°.

Baphiin, baphinitone, and substance (3) above referred to, are all coloured orange-yellow by sulphuric acid; with nitric acid an orange-red colour is obtained, which changes gradually to green.

In addition to the above-mentioned substances, barwood contains, according to Anderson, at least three colouring matters. Ether extracts from the wood two of these; one (*a*) which is less soluble, and which tenaciously adheres to the baphiin, and another (*b*) which is crystalline and is easily removed from it. When the extraction with ether is completed, alcohol will dissolve out a third colouring matter (*c*). All are insoluble in benzene, and give purple lakes with lead acetate, and purple solutions with alkalis.

O'Neill and Perkin (*l.c.*) worked up barwood by the same methods they had previously applied to sanderswood, and isolated a colouring matter, corresponding with the santalin of this latter, This, which consisted of a chocolate-red powder, possessed the formula $C_{22}H_{16}O_5(OCH_3)_2$, and on heating commenced to soften at 240°, apparently decomposing, and at 270° had the appearance of a honeycombed carbonaceous mass. Its colour reactions are the same as those given by santalin, and it thus appears probable that the two compounds are identical.

When the crude colouring matter of barwood, dissolved in alcohol, is poured into ether the main bulk of the santalin is precipitated. The ethereal liquid now contains, in addition to a colouring matter resembling *deoxysantalin*, two crystalline substances identical with those previously stated by Wiedel (*l.c.*) as present in sanderswood. To isolate santal the ether solution is treated with hydrobromic acid to remove colouring matter, the colourless crystalline residue remaining after evaporation is washed with benzene, and recrystallised first from dilute and subsequently from absolute alcohol.

The analytical figures given by this compound agree with those obtained by Weidel, but methoxy determinations show that its formula is to be represented as $C_{15}H_9O_5(OCH_3)$, and not $C_8H_6O_3$, as proposed by this author.

Santal, which seems to be very similar to Anderson's baphic acid, melts at 222°–223°, is readily soluble in dilute alkali hydroxides, and sparingly so in absolute alcohol from which it crystallises in thin plates or flat needles. With alcoholic lead acetate it gives a colourless precipitate, and with alcoholic ferric chloride a violet-black colouration, although this, according to Weidel, is dark red. By the action of hydriodic acid santal is converted into *santol*, probably $C_{15}H_{10}O_6$, which consists of small colourless flat needles, m.p. 270°–273°. Its solution in dilute alkali hydroxide, at first colourless, rapidly develops a reddish-violet tint, and the liquid on acidification deposits yellow crystals. If the acid mixture is boiled these become colourless, apparently with regeneration of santol, for when collected and washed the product can again be made to produce the same changes. Santol thus appears to contain a lactone group. The hydrobromic acid liquid obtained during the isolation of the santal, was diluted with water, the precipitated colouring matter dissolved in a little ethyl acetate, the solution being allowed to evaporate spontaneously. Minute crystals were slowly deposited, and these were collected and digested with absolute alcohol to remove santal. This compound, evidently Weidel's substance $C_{14}H_{12}O_4$, and termed by O'Neill and Perkin *santalone*, is sparingly soluble in most organic solvents, and crystallises from alcohol in small red leaflets. It is soluble in dilute alkalis with a red colour, whereas alcoholic ferric chloride colours it a violet tint. As obtained by these latter authors its complete purity was doubtful, but the purest preparation obtained darkened about 280° and melted at 300°. Its true formula is probably either $C_{22}H_{13}O_4(OCH_3)_3$ or $C_{22}H_{15}O_4(OCH_3)_3$, and in case this is correct this compound has the composition of a *deoxysantalin monomethyl ether* with which its general properties are in harmony.

Ryan and Fitzgerald (Proc. Roy. Irish Acad. 1913, 5, 106), employing the following method, have isolated *homopterocarpin* from barwood. The ground material was percolated for a few days with warm alcohol, then with ether, and finally with chloroform. The residue obtained by evaporating these extracts was exhausted with ether, the ethereal solution washed with dilute alkali and then distilled. The product, when recrystallised from alcohol, formed colourless acicular crystals, m.p. 84°, and was identical with the baphinitone of Anderson and the homopterocarpin existing in sanderswood.

A fuller account of this compound, which possesses the formula $C_{17}H_{16}O_4$, is given in the article describing the latter dyewood. It is very probable, again, that the *baphinitin* described by Anderson as existing in barwood is pterocarpin. A. G. P.

BARYTA GREEN *v.* BARIUM.

BARYTES. Barite, or heavy-spar (from βαρύς, heavy); a common mineral consisting of barium sulphate ($BaSO_4$), and crystallising in the orthorhombic system. The name barytes is, however, sometimes loosely, but incorrectly, applied to include both this species and the mineral witherite ($BaCO_3$, *q.v.*), or these are occasionally referred to as 'sulphate of barytes' and 'carbonate of barytes' respectively. The reason for this confusion is that the two minerals are often mined together, although they are not always put to the same uses.

Barytes is frequently to be found as well-developed crystals, which vary considerably in their appearance and habit. They possess a perfect cleavage parallel to the base, and perpendicular to this are two prismatic cleavages parallel to the faces of the primitive rhombic prism, and inclined to one another at an angle of 78° 22½′. With these three directions of perfect cleavage, massive barytes sometimes presents a certain resemblance to calcite, and its hardness is also about the same (H.=3). The angles between the cleavages are, however, different; and, further, barytes may be readily distinguished from calcite by its heaviness (sp.gr. 4·5), and from both calcite and witherite by not effervescing with acid. The massive material is often white and opaque; but crystals are sometimes transparent and colourless, or with brownish, greenish, or bluish shades of colour.

Barytes is usually met with in veins, often in association with ores of lead. Some of the old lead-mines of the north of England, Derbyshire and Shropshire are now being reworked for barytes. A remarkable vein of barytes, consisting of pure white massive material with a thickness varying from a few inches to 16 feet, is extensively worked in the coal-measures at New Brancepeth Colliery, near Durham (L. J. Spencer, Mineralog. Mag. 1910, xv, 302). Beautiful crystallised specimens are abundant in the hæmatite-mines of west Cumberland, but, owing to the brown or yellow colour of this material, it is of no commercial value. A pure white granular barytes resembling marble in appearance is mined at Dunmanus Bay, in Co. Cork. Important deposits of the mineral are worked in the United States, Germany, Rhodesia, &c. Barytes occurs abundantly as a cementing material in Triassic sandstones in the Midlands of England (F. Clowes, 1889, 1890); and it has been recently suggested that this could be easily won by washing.

Barytes is mainly used in the manufacture of paints, not only of white paint, but as an inert body in coloured paints. Lithophone paint consists largely of barium sulphate with zinc oxide and sulphide. It is often suggested that barytes is used for adulterating various articles. Barium sulphide and carbonate are also prepared from barytes by roasting it with coal, and from the product, barium chloride, barium hydroxide, &c., are prepared. In preparing the crude barytes for the market, it is coarsely crushed and hand-picked; or when mixed with rock and dirt, these are separated by agitation (jigging) in water. Coloured impurities are sometimes extracted by steam-boiling with sulphuric acid. The purified material is kiln-dried and reduced to very fine white powder in a ball-mill provided with screens, or between millstones. The barytes flour so prepared stil consists of minute crystalline (cleavage) particles and it is this that gives the 'tooth' or adhesiv properties to the coarser barytes paints. Th finer qualities ('blanc fixe') are prepared from precipitated barium sulphate; and this is als used for dressing cloth and leather, and fo producing the smooth coating on 'art' papers

References.—For details of British occurrences, *see* Special Reports on the Minera Resources of Great Britain, vol. ii, Barytes an Witherite, Mem. Geol. Survey, 2nd ed. 1916 For the United States, and a general accoun with bibliography, *see* Mineral Resources of th United States, for 1915, U.S. Geol. Survey 1916; H. Ries, Economic Geology, New York 1916. L. J. S.

BARYTIC WHITE or **PERMANENT WHIT** or **BLANC FIXE** *v.* BARIUM; also PIGMENTS.

BARYTO-CELESTITE *v.* BARIUM.

BARYTOCALCITE, Barium and calciu carbonate, $BaCO_3 \cdot CaCO_3$, crystallising as prismatic and blade-shaped crystals in the monoclinic system. There are good cleavages i three directions (the basal plane and a prism) and curiously the angles between these ar near to the angles between the three cleavage of calcite. The composition is the same as tha of alstonite (*q.v.*), but whilst alstonite is a isomorphous mixture of barium and calciu carbonates, barytocalcite is a double salt. Th mineral is white or colourless, and has a vitreou lustre. Sp.gr. 3·65; hardness 4. Apart from a doubtful record from Glamorganshire, th mineral has been found only in the old Blagill or Bleagill,[1] lead mine, near Alston, in Cumberland. Here it occurs in considerable quantity and was at one time mined as a 'low-grad witherite.' Large blocks of massive material with crystal-lined cavities may still be found lying outside the mine. Although containing less barium carbonate (66·3 p.c.) than witherite, it may prove to be of commercial value. L. J. S.

BASALT. A group of volcanic rocks of basic composition (SiO_2 45–55 p.c.), corresponding with the plutonic gabbros. The name is one of the oldest in petrography, being of Ethiopian origin and said to signify a stone that yields iron. Many of the ancient Egyptian and Assyrian monuments were carved in basalt, and it is the material of the famous Rosetta stone. The term is used in rather different senses. A quarryman often recognises amongst the difficultly-worked igneous rocks only granite and basalt, and commonly any dark-coloured fine-grained rock is included under the term basalt or trap-rock. Also petrographers are not agreed amongst themselves as to the limitations of the term. Strictly, it should be applied to a rock which has flowed as a lava on the earth's surface, and is composed of a basic plagioclase-felspar (bytownite or labradorite) and augite, together with small amounts of magnetite and ilmenite, and sometimes glassy (uncrystallised) material in the groundmass. Sometimes porphyritic crystals are present, but usually the component minerals can only be recognised when thin sections of the rock are examined under the microscope; the rock appearing compact and homogeneous to the unaided eye. Other minerals are sometimes present, particularly olivine, and we then have the varieties olivine-basalt, hornblende-basalt, &c. In a less common type of alkali-basalt the felspars are partly or wholly replaced by felspathoid minerals (nephelite, leucite, and melilite). When the felspars are wholly replaced we have the varieties nephelite-basalt, leucite-basalt, &c.; and when both felspar and felspathoid are present the rock is termed tephrite or basanite, according as olivine is absent or present. A leucite-basanite, then, consists of plagioclase, augite, olivine, and leucite. Analyses of some of these types of basaltic rocks are given below: I, average of 198 analyses of typical basalts, including olivine-basalts; II, basalt from Disko Island, west Greenland; III, olivine-basalt from the Isle of Skye, Scotland; IV, leucite-tephrite from Rome; V, leucite-basalt from Highwood Mountains, Montana.

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[1] A corruption of the German Blei (lead), and a relic of the German miners employed in the Cumberland mines in the reign of Queen Elizabeth.

	I.	II.	III.	IV.	V.
SiO_2 .	49·06	47·11	46·61	50·25	47·98
TiO_2 .	1·36	0·78	1·81	0·57	0·58
Al_2O_3 .	15·70	14·33	15·22	21·41	13·34
Fe_2O_3 .	5·38	4·88	3·49	1·76	4·09
FeO .	6·37	11·06	7·71	1·82	4·24
MnO .	0·31	0·21	0·13	—	trace
CaO .	8·95	9·12	10·08	4·48	9·32
MgO .	6·17	8·45	8·66	0·31	7·01
Na_2O .	3·11	1·91	2·43	5·16	3·51
K_2O .	1·52	0·20	0·67	11·32	5·00
H_2O .	1·62	1·52	3·17	0·96	2·10
P_2O_5 .	0·45	0·29	0·10	0 12	1·03

As a consequence of their volcanic origin, basalts often exhibit a vesicular texture, owing to the expansion of water-vapour in the rock before consolidation; and in these cavities secondary minerals (chalcedony, calcite, and zeolites) are often deposited. A well-marked columnar structure, often on a large scale, is a common character; *e.g.* at the Giants' Causeway in Co. Antrim, the Staffa caves in the Western Isles of Scotland, and in the Linz basalt quarry on the Rhine. It is a dense, black rock weathering to brown or dark green. Sp.gr. 2·8–3·1. The crushing strength is high (2000–3000 tons per square foot); the absorption for water low (about 1 p.c.); and the conductivity for heat considerable, buildings of basalt being for this reason cold in winter and hot in summer.

Basalts are of world-wide distribution, and sometimes cover enormous tracts of country; *e.g.* the Arctic region extending to the Western Isles of Scotland, and the north of Ireland, the Deccan traps of India, and the lava-fields of Washington, Oregon, and Idaho. The rock is quarried at many places for road-metal and paving stones, and on the Continent as a building stone. But it is to be remembered that much of the rock quarried under the name of basalt is included by petrographers under other terms, particularly dolerite and diabase (*q.v.*). The types of alkali-basalts are less widely distributed, but are abundant in central Italy, in the neighbourhood of Rome and Vesuvius, and are known in Germany, Bohemia, Wyoming, Montana, and Brazil. These are of importance on account of their high content of potash (analyses IV and V above). L. J. S.

BASE OILS *v.* Oils and Fats.

BASIC BESSEMER STEEL *v.* Iron.

BASILICON. *Resin cerate.* A mixture of oil, wax, and resin.

BASIL OIL *v.* Oils, Essential.

BASLE BLUE *v.* Azines.

BASSIA MAHWA or MOWRAH FLOWERS. The flowers of *B.* (*Illipé*) *latifolia* (Roxb.) or Mahwa, a tree growing to the height of 60 feet, very abundant in Central India, are very succulent, and fall from the tree in large quantities every night, a single tree affording from 200 to 400 lbs. of flowers in a season, which lasts during March and April. They are used as an article of food, both cooked and raw. By fermentation and distillation they yield upwards of 6 gallons of proof spirit per cwt. It is of superior quality, and when the operations have been carefully performed, is very much like good Irish whisky, having a strong smoky and rather fœtid flavour, which disappears with age.

They have also been used as a cattle food with success. It is said that the flesh of pigs and other animals is much improved, acquiring a delicate flavour.

The dried flowers have been recommended as a source of sugar. Negri found in them 57·9 p.c. of glucose, yielding 26·74 p.c. of alcohol on distillation (Rev. Chim. Med. Pharm. 2, 384; *cf.* von Lippmann, Ber. 1902, 35, 1448).

BASSIA OILS. Under this name are comprised a number of oils belonging to the genus *Bassia*. The most important oils (or fats) derived from *Bassia* species are: Mowrah Seed Oil, Illipé Butter, Shea Butter, Njave Oil, and Phulwa Butter. For a description of the fats derived from the kernels of different species of Bassia, *see* Bull. Imp. Inst. 1911, 9, 228.

Mowrah Seed Oil is the fat obtained from the seeds of *Bassia latifolia* (Roxb.) (*Illipé latifolia*, Roxb. or Engler; *Bassia villosa*, Wall.), a tree widely distributed in the northern provinces of India, and especially in Bengal. The tree is frequently cultivated in East India, and forms small plantations; but even under the incentive of modern demand for a solid fat, the cultivation of the Mowrah Seed tree for the production of fat is not likely to be taken in hand in the near future. The tree gradually disappears towards Calcutta, and is only sparingly met with in the Madras presidency, where its place is taken by *Bassia longifolia* (*see* below).

The kernels are 1-2 cm. long, and are enclosed in a light-brown shiny husk. The seeds are very similar in appearance to those of *Bassia longifolia*, with which they are frequently confounded, much as the fat obtained from both species is frequently confounded in commerce. This is partly due to the fact that the two kinds of fats are mixed together when exported to Europe, a practice which is greatly favoured by the fact that both species are known to the natives under such similarly sounding names as Illipi, Elupa, Katillipi.

The kernels dried at 100° contain, according to Valenta:

Fat extracted (by petroleum ether) .	51·14
,, soluble in absolute alcohol . .	7·83
Tannin	2·12
Bitter principle, soluble in water . .	0·60
Starch	0·07
Vegetable mucilage	1·65
Albuminous substances soluble in water	3·60

Extractive substances soluble in water	15·59
Insoluble proteins	4·40
Total ash	2·71
Fibre and loss	10·29

In its fresh state the fat is yellow; on exposure to the air the colouring matter is bleached. The oil can also be bleached chemically, as has been done by the author, on a large scale.

The fat has the sp.gr. of 0·9175 at 15°, melts at about 25·3°–30°, and solidifies at 18·5°–22°.

The fat has a bitter aromatic taste and a peculiar odour. The iodine value of the fat is 50, thus indicating a considerable amount of oleic acid. The chief constituent of the solid fatty acid is palmitic acid; arachidic acid is absent; stearic acid (13–25 p.c.) has been found to occur in specimens examined by Menon. The saponification value of the commercial fats is slightly lower than that of fats having the constitution due to the fatty acids named, owing to a somewhat high proportion of unsaponifiable matter, viz. 2·34 p.c. The fat is prepared in India in a crude manner, and the cakes are used as manure. Owing to a bitter principle (saponin) contained in the cakes, they are unfit as food for cattle. Nevertheless, the cake is frequently added as an adulterant to the so-called 'native linseed cake,' which, under this misleading name, has latterly found extensive sales on the Continent. The seeds and the oil have become an important article of commerce. They are imported to Europe in irregular quantities, and are chiefly used in the soap and candle industries. Endeavours have also been made to convert the fat into an edible fat. In India, Mowrah seed oil is largely used as an edible fat under the name 'Dolia oil,' and as a medicinal oil in the treatment of skin diseases under the name 'Mo oil.'

Illipé Butter is obtained from the seeds of *Bassia longifolia* (Linn.), a tree indigenous to the southern part of India; a variety of this *Bassia* species is known as *Illipé malabarica* (König), in the Western Ghats from Kanara to Travancore and the Anamalais, where the tree is found at an altitude of about 4000 feet. The seeds bear a close resemblance to those of *B. latifolia*, but are mostly 3–4 cm. long, and less rounded than the seeds of *B. latifolia*. The average weight of one seed is 1·4 grms. The kernels form 75 p.c. of the seeds, and contain 50–55 p.c. of a white to light-yellow coloured fat. The fat closely resembles Mowrah seed oil, but differs from it by its lower solidifying and melting points; in correspondence therewith the iodine value of the fat is 58–64, *i.e.* higher than that of *B. latifolia*. The fat contains from 12 to 20 p.c. of stearic acid; arachidic acid is absent (Menon).

Illipé seeds are imported into France and England (usually in admixture with Mowrah seeds), where the fat is expressed for use in candle-making. The proposal to employ the fat as a chocolate fat appears to be due to the confounding of true Illipé seeds with seeds from the Malayan States, erroneously described in the market as 'Illipé nuts.'

Owing to the fact that the term 'illipé' is applied to many fats, it has been suggested by Revis and Bolton (Fatty Foods, 183) that the confusion might be prevented by adopting the name 'Latifolia' and 'Longifolia fat' for the products of the preceding species.

Shea Butter is the fat obtained from the seeds of *Bassia Parkii*, De C. (Hassk.), *Butyrospermum Parkii*, [G. Don] (Kotschy), a tree belonging to the *Sapotaceæ*. The tree was first described by Mungo Park, who found it in the kingdom of Bambara. Hence the fat was known as Bambara fat and also Bambooi fat. Other native names are Galam Butter, Bambuk Butter, and, in French West Africa, Karité Oil. The Shea Butter tree, or Karité tree, which resembles in appearance the American oak, and grows to a height of about 40 feet, occurs in enormous quantities on the West Coast of Africa, and through the centre of Africa in the French and English Soudan. It is especially abundant in the middle basin of the Niger, and is as characteristic of the region of the middle Niger as is the palm tree of the lower reaches of the rivers and of the coast line. The Shea nut has the size and shape of an ordinary plum; the outer shell of some specimens is covered with fine fibres, whereas the shell of nuts coming from the middle Niger district has a polished surface. Owing to the wide distribution of the tree, the different specimens of nuts and fats exported to Europe show characteristic differences. A special variety appears to be represented by the specimen known as *Bassia niloticum* (Kotschy et Chevalier). The seeds contain from about 32 to 44 p.c. of fat, corresponding to about 49 to 59 p.c. in the kernel, the amount varying with the origin of the seed. The natives extract the fat by pounding the kernels and boiling the paste with water. The fat rises to the surface and is skimmed off into large calabashes, in which it is carried to the river for shipment. Since little care is taken in the preparation of the exported oil, much of the shea butter sent to Europe had at one time a dark-grey colour, which was considered to be characteristic of shea butter. The fat used by the natives for their own purposes is, however, prepared in a more careful manner, made into cakes and wrapped round with leaves, so that it may keep. This fat is of a white colour, and keeps well for several months.

Shea butter plays a very important part in the economy of the natives as an edible fat, and also as a burning oil, and for cosmetic purposes. Attempts have been frequently made to ship the fat and the nuts in bulk to Europe. Owing partly to the careless preparation, and partly to a resinous substance dissolved by the fat, shea butter contains considerable amounts of unsaponifiable matter which imparts to the fat an indiarubber-like taste. This large amount of unsaponifiable matter (5–9 p.c.) has prevented the extensive employment of the fat for soap-making purposes; but methods for removing part of the unsaponifiable matter have been devised. The fat is also used as a candle material, and, in the refined form, as a substitute for lard.

The specific gravity of the fat is 0·9177; its melting-point varies from 25° to 28°. Owing to the considerable amount of unsaponifiable matter, the saponification value varies from 171 to 192. The iodine value varies from 56 to 63, so that the proportion of oleic acid in the fat may be estimated at about 60 p.c. The author found in a number of shea butters from 33 to 37 p.c. of stearic acid. The remainder of the fatty acid appears to consist of lauric acid (Southcombe, J. Soc. Chem. Ind 1909, 499).

Njave Oil, *Njave Butter, Nari Oil, Noumgou Oil, adjab Oil*, is the oil obtained from the seeds of *Mimusops Njave* (De Lanessan), syn. *Bassia Djave* (De Lanessan); *Bassia toxisperma* (Raoul); *Tieghemella africana* (Pierre); *Baillonella toxisperma* (Pierre); *Baillonella Djave* (Pierre); *Tieghemella Jollyana* (Pierre), a tree belonging to the family of the *Sapotaceæ*. The wood of this tree is known in commerce as 'Cameroon mahogany.' The tree is indigenous to West Africa, the Cameroons, Gaboon, and Nigeria, and furnishes, like most trees belonging to the *Sapotaceæ*, guttapercha. The fruits are known in commerce as 'Mahogany nuts'; in the Gold Coast Colony they are termed 'Abeku and 'Bako' nuts. The weight of the nuts varies between 10 and 21·6 grams, one-third of which is made up by the shell. The kernels contain 43–64 p.c. of a white fat, which the natives (the *Jaundes* and the *Ngumbas*) prepare by drying the seeds over fire and breaking the shell with stones. The kernels are then pounded in a mortar or comminuted by rubbing between stones. The mass is next boiled out with water, the fat is skimmed off by hand, and freed from the bulk of water by squeezing between the hands, and then subjecting it to a somewhat stronger pressure in baskets, by heaping stones on the mass. By this process an extremely poisonous saponin, contained in the fresh seeds, is completely removed, so that the fat can be used for edible purposes. In case the seeds should be expressed on a large scale the press cakes would retain the poisonous substance, and hence be valueless as a feeding cake (Der Tropenpflanzer, 1910, 29), unless the saponin be removed completely by boiling out with water. But even if this process were feasible, a considerable amount of nutritive substances would be removed thereby. The economic prospects of the seeds are, therefore, still doubtful; nevertheless, the exports from the German Cameroons have increased from 3 tons in 1906 to 183 tons in 1908. The fat solidifies at about 21°, and has an iodine value of about 65.

Phulwa Butter is the fat expressed from the kernels of *Bassia* (*Illipé*) *butyracea* (Roxb.), the 'Indian butter tree,' which is indigenous to the Himalayas. The seeds, known as 'phulwara,' are smaller and thinner than those of *B. latifolia* and *longifolia*. The average weight of one seed is one gram. The kernels form 67·5 p c. of the total seed; they contain 50–66 p.c. of a white fat, having the consistence of lard. Phulwa Butter is one of the most important foodstuffs amongst the natives of the North-West Provinces, on account of its pleasant odour and agreeable taste, and is frequently used to adulterate Ghee. The butter is also highly valued by the natives as an ointment when properly perfumed. The melting-point of the fat is 39°, and its iodine value 42°. Stearic acid is absent (Menon).

Less-known Bassia Oils are: *Payena Oil* or *Kansive Oil*, from *Payena oleifera* (Chemical Technology and Analysis of Oils, Fats, and Waxes, ii. 800), and *Katio Oil*, from *Bassia Mottleyana*, which solidifies at 14°–15° and has an iodine value of 63–65 (Brooks, Analyst, 1909, 207). J. L.

BASSORIN *v.* Gums and Gum Tragacanth.

BASSWOOD OIL. An oil from *Tilia americana*, resembling cotton-seed oil, and consisting of glycerides rich in butyric acid (Wiechmann, Amer. Chem. J. 1895, 17, 305).

BAST FIBRES. Elongated narrow plant-cells that form strengthening tissue in stems and leaves, especially in connection with the fibro-vascular bundles, but not belonging to the wood. The raw material, bast or bast-like fibre, used for textile purposes or for the manufacture of paper, ropes, and the like, is of varied nature and source, but is always characterised by the abundance in it of bast fibres. It may be composed of a number of fibro-vascular bundles, or one such bundle (*e.g.* coco-nut fibre), or part of fibro-vascular bundle (*e.g.* fibre from leaves of monocotyledons), or merely a bundle of true bast fibres (from the fibro-vascular bundles or bark of dicotyledonous stems).

A typical bast fibre has a thick wall, with slit-like oblique pits, and a relatively small lumen. The ends usually taper to fine points, but may be blunt or even branched. The cell-wall varies in thickness in different species, from comparatively thin to extremely thick, and may vary in the same fibre, so that the lumen is alternately wider and narrower. When the wall is very thick the lumen is reduced to a line, and may be locally evanescent. There are similar differences in the width, length, and strength of the raw material and individual bast fibre. The colour varies from the usual whitish-grey or green or yellow, through yellow and brown to black.

The cell-wall is mainly composed of celluloses and in certain species (flax, *Calotropis gigantea*, and others) is entirely soluble in ammoniacal cupric oxide, and gives the colour reactions for celluloses; but the bast fibres of certain other species (jute, hemp, esparto, and others) show lignification, and give corresponding colour reactions.

Bast fibres in commercial use are mainly obtained from comparatively few alliances and families of dicotyledons, and genera of monocotyledons, namely, Malvales (Malvaceæ), Tiliaceæ, Sterculiaceæ, Urticales (Moraceæ, Urticaceæ, Ulmaceæ), Leguminosæ, Linaceæ, Apocynaceæ, and Asclepiadaceæ, Boraginaceæ; *Agave* and *Fourcroya*, *Aloë*, *Bromelia*, *Sanseviera*, *Musa*, *Stipa*, *Pandanus*, and several palms. (*See* articles on any of these, and Jute and Hemp. For a full authoritative account of vegetable fibres, *see* Wiesner, Die Rohstoffe des Pflanzenreichs, 1903, Bd. ii. 167–463.)

BASTNÄSITE. A fluocarbonate of cerium-metals (CeF)CO_3, long known as small yellowish masses with greasy lustre embedded between allanite crystals at the Bastnäs mine, Riddarhyttan, Sweden. It has also been observed as an alteration product of tysonite (CeF_3) in the granite of the Pike's Peak region in El Paso Co., Colorado. Recently large masses have been found in Madagascar in the weathered debris of pegmatite at Torendrika to the east of Ambositra and near Antsirabe. These have the form of rough hexagonal prisms of a yellow to reddish-brown colour. Some crystals show an separation parallel to the basal plane on which the lustre is then pearly, otherwise it is greasy in character. The crystals are optically uniaxial and positive. Sp.gr. 4·948. The mineral is difficultly attacked by hydrochloric acid, but is decomposed by sulphuric acid, with evolution of carbon dioxide and fluorine. It is infusible before the blowpipe. L. J. S.

BATATAS, or Sweet Potatoes, the tubers of *Ipomœa batatas* or *Batata edulis*, a convolvulus-like plant, usually with purple flowers, growing freely in tropical and sub-tropical countries. The tubers are sometimes of great size—up to 12 lbs. or more in weight.

It can be propagated by cuttings or by the tubers, and, once established, often yields several crops in succession. An average crop is about 5 tons per acre. Light friable soils are most suitable.

Average composition of sweet potatoes and their vines:

	Water	Protein	Fat	Soluble carbohydrates	Fibre	Ash
Tubers .	71·1	1·5	0·4	24·7	1·3	1·0
Vines .	41·6	7·6	2·1	29·3	13·6	5·8

A more detailed analysis of the tubers as grown in Monte Video, is given by Saco (Bied. Zentr. 1883, 337):

Water	Protein	Glucose	Mucilage	Pectic acid	Starch	Fibre	Ash
67·0	0·56	0·3	1·15	1·27	13	10	1·0
to	to	to			to	to	
68·2	0·64	4·0			15	17·8	

The sweet potatoes are largely used as food, and also in the manufacture of alcohol.

According to Stone (Ber. 1890, 23, 1406), they contain from 1·5 to 2·0 p.c. of cane sugar, and baking converts the starch into the soluble form and hydrolyses the cane sugar. The tops of sweet potatoes are greedily eaten by farm animals, but should be used with care, since they sometimes contain a poisonous cyanogetic glucoside. Amounts of hydrocyanic acid, varying from 0·014 to 0·019 p.c. of the green material, have been found. Sweet potato vines have often proved fatal to pigs in Queensland.

Hasselbring and Hawkins (J. Agric. Research, 1915, 5, 543) state that the amount of sugar in the tubers is comparatively small until after they are harvested; but when they are cut off from connection with the leaves, the starch is transformed, first, into reducing sugars, and ultimately into sucrose. The reaction proceeds rapidly at high temperatures, but soon reaches an end-point, while at lower temperatures the change is slower, but ultimately proceeds further. H. I.

BATH BRICK. A brick made from deposits of silicious and calcareous earth at Bridgwater, Highbridge, and elsewhere, and used for polishing metals.

BATH-METAL. An alloy of copper and zinc, containing a larger proportion of copper than ordinary brass, viz. 83 p.c. copper to 17 p.c. zinc; sp.gr. 8·451; fracture crystalline, and colour yellowish-red.

BATHYCHROME *v.* Colour and Chemical Constitution.

BATIST. A material consisting of cotton impregnated with caoutchouc on one or both sides, largely used in the French army for compresses and antiseptic dressings.

BAUXITE. A clay-like aluminium hydroxide first noticed by P. Berthier in 1821 (*alumine hydratée des Beaux*), and named beauxite by A. Dufrénoy in 1847, and bauxite by H. Sainte-Claire Deville in 1861; this name being from the village Les Beaux, or Les Baux, near Arles, dep. Bouches-du-Rhône, in the south of France, where the material was found. This material came to be regarded as a mineral species with the composition $Al_2O_3,2H_2O$, corresponding with Al_2O_3, 73·9; and H_2O, 26·1 p.c.; that is, intermediate between the definite crystallised species diaspore (Al_2O_3,H_2O) and hydrargillite or gibbsite ($Al_2O_3,3H_2O$). It, however, varies widely in composition, owing to intermixture with quartz-sand, clay, and iron hydroxide, and it passes insensibly into clays, iron-ores, and laterite. The variations shown by different analyses are: Al_2O_3, 30·3–76·9; H_2O, 8·6–31·1; Fe_2O_3, 0·1–48·8; SiO_2, 1·1–41·5; TiO_2, 1·6–4·0 (from table of analyses quoted by G. P. Merrill, The Non-metallic Minerals, New York, 1910). (For other analyses of French bauxite, *see* H. Arsandaux, Compt. rend. 1909, cxlviii, 936, 1115; Bull. Soc. franç. Min. 1913, xxxvi, 70.)

The material never shows any indications of crystalline structure, being always compact or earthy, or often with a concretionary (pisolitic or oolitic) structure. In colour it ranges from white, through creamy and yellow, to brown and deep red. Under the microscope it shows only optically isotropic, flocculent grains. Bauxite is thus no doubt a mixture of colloidal aluminium hydroxides (for which the mineralogical name kliachite has been proposed by F. Cornu, 1909, and sporogelite by M. Kišpatić, 1912) with various iron hydroxides, clays, &c., and possibly also the crystalloids diaspore and hydrargillite; and it is thus rather of the nature of a rock than a simple mineral.

In its mode of occurrence, and no doubt also in its mode of origin, it also shows wide differences. The extensive deposits in the south of France have the form of beds interstratified with limestones of Cretaceous age, or of irregular pockets in the limestone. Those of Co. Antrim and of the Vogelsberg and Westerwald in Germany, are associated with laterite, and are interbedded with basaltic lava-flows. In Arkansas the bauxite deposits occur only in Tertiary areas in the neighbourhood of eruptive syenites, while in Alabama and Georgia they overlie ancient sedimentary rocks. The frequent presence of pisolitic structures in the material and its association with limestones, has led to the suggestion that bauxite has been deposited by hot springs containing aluminium salts in solution (probably aluminium sulphate from the decomposition of pyritous shales), where these have come into contact with limestone rocks. On the other hand, the material associated with laterite and basalt has, no doubt, been produced by the weathering under special conditions (the agency of bacteria has been suggested) of basalt or of other igneous and crystalline rocks. (For papers on the constitution of bauxite and laterite, *see* M. Bauer, Jahrb. Min. 1898, ii., 163; T. H Holland, Geol. Mag. 1903, 59; A. Lacroix, Nouv. Archives du Musée, Paris, 1914, v, reviewed by L. L. Fermor, Geol. Mag. 1915; G. A. J. Cole, The Interbasaltic Rocks (Iron Ores and Bauxites) of North-East Ireland, Mem. Geol. Survey, Ireland, 1912; H. Ries, Economic Geology, New York, 1916; W. C. Phalen, Mineral Resources of the United States, for 1915, 1916, ii, 159.)

The alum-clay or bauxite mined in Co. Antrim is all sent to the aluminium works at Foyers and Kinlochleven in Scotland. In France the present source of supply is mainly in dep. Var; and in America the production is confined to the states of Alabama, Georgia, and Arkansas. The French bauxite is roughly divided into three classes: (1) white bauxite, with 60 p.c. alumina, not more than 4 p.c. iron, and no silica,—this being used for the manufacture of aluminium salts and alum; (2) red bauxite, with 60 p.c. alumina and 3 p.c. silica,—used for the manufacture of aluminium; (3) a special kind of white bauxite, with 45 p.c. alumina, a trace of iron, and much silica,—used for making refractory bauxite bricks. The greater part of the material is used in the manufacture of aluminium, but in America large quantities are fused in the electric furnace to produce artificial corundum, which, under the name of *alundum*, is largely used as an abrasive agent. L. J. S.

BAVALITE *v.* Thuringite.

BAY, BAY OIL *v.* Laurus nobilis.

BAYBERRY TALLOW *v.* Waxes.

BAYER'S ACID, 2-Naphthol-8-sulphonic acid. *V.* Naphthalene.

BAY-LEAF OIL *v.* Oils, Essential.

BAY-SALT *v.* Sodium chloride.

BAZILLOL. Trade name for a preparation of crude carbolic acid. Used as a disinfectant.

BDELLIUM *v.* Gum resins.

BDELLIUM RESIN *v.* Resins.

BEAN. The name given to many seeds which resemble in size and shape the ordinary kidney bean. Thus the seeds of coffee, cocoa, castor, &c., are often known as 'beans.' Usually, however, the term is restricted to seeds of various *leguminosæ.*

The most important species of beans are:

(1) Adzuki beans (*Phaseolus radiatus*).

(2) Field or horse beans, of which the broad bean is a variety (*Vicia faba*).

(3) French or kidney bean (*Phaseolus vulgaris*).

(4) Java or Lima bean (*Phaseolus lunatus*)

(5) Soy or Soja bean (*Glycine hispida* or *Soja hispida*).

(6) Velvet bean (*Mucuna utilis*).

(7) Carob or locust bean (*Ceratonia siliqua*).

In chemical composition beans are remarkable for the large proportion of albuminoid matter which they contain. They thus possess high nutritive value as foods.

In some cases the seed only is eaten, either green as in broad beans, or dried as in haricot beans, which are a variety of *Phaseolus vulgaris.* In others, *e.g.* in the kidney bean, the whole pod, in the unripe condition, is eaten; whilst in the case of the carob bean, the dried pod rather than the seeds is the valued product. The velvet bean is usually grown for its foliage, either for making into hay for cattle or for green manuring.

In the following table are given analyses of various beans, as far as possible of the products as they are usually consumed as food:—

—	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Water	13·6	87·3	11·1	68·5	14·4	10·0	16·0	9·3	19·7
Protein	23·1	2·2	15·9	7·1	23·9	33·2	17·2	13·3	5·5
Fat	2·3	0·4	1·8	0·7	1·6	17·5	2·2	2·6	0·8
Soluble carbohydrates . .	56·6	9·4	67·1	22·0	49·3	30·2	28·9	39·4	39·6
Crude fibre	3·9				7·5	4·4	29·5	27·6	7·8
Ash	3·5	0·7	4·1	1·7	3·2	4·7	6·2	7·8	2·5
Undetermined	—	—	—	—	—	—	—	—	24·1

(1) *Phaseolus vulgaris*, dried seeds, as used as haricot beans.

(2) *Phaseolus vulgaris*, green pods, as used as kidney beans.

(3) *Phaseolus lunatus*, dried.

(4) „ „ green.

(5) *Vicia faba*, dried.

(6) *Soja hispida*, dried seeds.

(7) „ „ hay.

(8) *Mucuna utilis*, hay.

(9) *Ceratonia siliqua*, whole pod.

The proteins of beans were thought to consist largely of legumin, or 'vegetable casein,' first obtained from them by Einhof in 1805, but Hoppe-Seyler has shown that the vegetable casein is produced by the action of the alkali used in extraction upon the globulins and albumins present in the seeds.

The proteins of *Phaseolus vulgaris* are chiefly phaseolin, a globulin containing 16·45 p.c. N and 0·5 p.c. S, and phaselin (Osborne, J. Amer. Chem. Soc. 1894, 16, 633). In *Phaseolus radiatus* are present phaseolin and another globulin containing 16·31 p.c. N and 0·88 p.c. S (Osborne and Campbell, J. Amer. Chem. Soc. 1897, 19, 509). In *Vicia faba*, the same investigators found legumin, vicilin, legumelin, and a proteose (same Journal, 1898, 20, 393). In *Soja hispida* they found, as the chief proteid, a globulin resembling legumin, but containing twice as much sulphur, for which they propose the name glycinin. Legumelin, a trace of a proteose, and a globulin, probably identical with phaseolin, were also present (*l.c.* 20, 419).

The nitrogen-free extract of soja beans contains the following substances (Street and Bailey, J. Ind. Eng. Chem. 1915, 7, 853); galactans 4·86 p.c.; pentosans, 4·94 p.c.; organic acids (as citric acid), 1·44 p.c.; invert sugar, 0·07 p.c.; sucrose, 3·31 p.c.; raffinose, 1·13 p.c.; starch, 0·50 p.c.; cellulose, 3·29 p.c.; hemicelluloses, 0·04 p.c.; dextrin, 3·14 p.c.; waxes, tannins, &c. (by diff.), 8·60 p.c. The same investigators found soja beans to contain the following enzymes: urease, amylase, a glucoside-splitting enzyme, a protease, a peroxydase, and a lipase.

According to Fleurent (Compt. rend. 1898, 126, 1374), bean flour contains 31 p.c. of nitrogenous matter, comprising legumin, 18·9 p.c.; vegetable albumin, 0·2 p.c.; glutenin, 9·5 p.c.; and gliadin, 2·4 p.c.; and has been used to add to wheaten flour, since the addition of 2 or 3 p.c. to the latter increases the ratio of glutenin to gliadin in the mixture, and thus in many cases improves the flour for bread making. The flour made from haricot beans contains starch as ovoid grains with distinct elongated or fissured hila, and square or rectangular cells containing prismatic crystals of calcium oxalate.

The fat of beans contains choline, cholesterol, and glycerides of valeric, oleic, and palmitic acids, but no stearic acid (Jacobson, Zeitsch. physiol. Chem. 1889, 13, 32). According to Kosutany (Landw. Versuchs-Stat. 1900, 54, 463), bean oil resembles olive oil in appearance, has a sp.gr. of 0·967, Reichert-Messel number 2·46, iodine number (Hübl.) 119·9, and contains much lecithin and sulphur. Stanek (Zeitsch. physiol. Chem. 1906, 48, 334) found both betaine and choline in horse beans.

Several varieties of beans contain a cyanogenetic glucoside. In *Phaseolus lunatus*, Dunstan and Henry (Proc. Roy. Soc. 1903, 72, 285) found a glucoside which they named phaseolunatin $C_{10}H_{17}O_6N$, yielding dextrose, prussic acid, and acetone on hydrolysis. The wild plant contains it in much larger quantity than the cultivated one. From haricot beans Tatlock and Thomson (Analyst, 1906, 31, 249) obtained from 0·001–0·009 p.c. of hydrocyanic acid. Most of the cyanogen compound, and the whole of the enzyme which hydrolyses it, are destroyed by boiling.

The carob or locust bean is remarkable for the large amount of sugar (cane sugar 23 p.c., glucose 11 p.c.) contained in the pod, while the seed contains a carbohydrate, caroubin, a white, spongy, friable substance, of the same composition as cellulose (Effront, Compt. rend. 1897, 125, 38), which yields in contact with water a very syrupy liquid or jelly, 3 or 4 grams of the substance being sufficient to convert a litre of water into a thick syrup. Caroubin might be used with advantage in the preparation of nutrient media for bacteriological work.

It has been introduced under the name of 'tragasol' as a gum for sizing, colour printing and dyeing (J. Soc. Chem. Ind. 1894, 410, and 1896, 112).

Effront (Compt. rend. 1897, 125, 309) states that by hydrolysis, either by dilute acids or the enzyme caroubinase, present in the seeds, caroubin yields a sugar, which he calls caroubinose, resembling dextrose, but with lower rotatory power.

Van Ekenstein (Compt. rend. 1897, 125, 719), however, finds this sugar to be identical with *d*-mannose. So, too, Bourquelot and Herissey find that the action of dilute acid upon the carob seed yields a mixture of mannose and galactose so that carubin apparently consists of mannans and galactans (Compt. rend. 1899, 129, 228 and 391). For analyses of commercial carobs *v.* Balland, J. Pharm. chim. 1904, 19, 569.

All species of beans, like other leguminosæ, serve as hosts for the tubercle-forming, nitrogen fixing organisms (*Bacillus radicocola*), and thus, under suitable conditions, are independent of supplies of combined nitrogen in the soil. Beans are therefore sometimes used for enriching soils in combined nitrogen, being employed for green manuring, though the root *débris* of a crop of beans, even after the removal of the seed and haulms, often effects this object to a considerable extent. H. I.

BEAN OIL. *See* SOYA BEAN OIL.

BEARBERRY LEAVES. The dried leaves of *Arctostaphylos uva-ursi* (Spreng).

BEBEERINE (*beberine*, *bibirine*) is a name which has been applied variously.

1. Maclagan (Annalen, 1843, 48, 106; with Tilley, 1845, 55, 105) first applied it to the amorphous ether-soluble alkaloid of bebeeru bark (*Nectandra Rodiei*, Hook.), to which the formula $C_{35}H_{20}O_6N$ ($C = 6$; $O = 8$) was attributed. This base was accompanied by another amorphous alkaloid, sipeerine, which was insoluble in ether, whilst bebeeru wood contained a third amorphous alkaloid, nectandrine $C_{20}H_{23}O_4N$ (Maclagan and Gamgee, Pharm. J. 1869-1870, [ii.] 11, 19).

2. It was applied later to the total alkaloids of bebeeru bark, the sulphate of which was official in the B. P. 1885, and was used as a febrifuge, as a substitute for quinine.

3. Bebeerine (from bebeeru bark) has been stated to be probably identical with the alkaloids of true pareira root (*Chondodendron tomentosum*, Ruiz. and Pav.), with buxine, contained in *Buxus sempervirens* (Linn.), and with the pelosine of *Cissampelos Pareira* (Linn.), but the evidence of identification is inconclusive. It has led, however, to the use of the term bebeerine for alkaloids isolated from *Chondodendron tomentosum* by Scholtz (Arch. Pharm. 1898, 236, 530; 1906, 244, 255) and Faltis (Monatsh 1912, 33, 873). Scholtz' bebeerine $C_{18}H_{21}O_3N$ crystallises from methyl alcohol in colourless prisms, m.p. 214°, $[\alpha]_D -298°$ in alcohol, forms crystalline salts, is phenolic, and contains one ·OMe and one ·NMe group. Faltis has described *β* bebeerine, amorphous, m.p. 142°–150°, $[\alpha]_D +28·6°$ in alcohol, $-24·7°$ in pyridine; *iso*bebeerine, rhombic needles, m p 290°, optically inactive; and bebeerine-B, $C_{22}H_{23}O_5N$, yellow powder, m.p. 220°, $[\alpha]_D +56·7°$ in pyridine. To *β*- and *iso*bebeerine, Faltis attributes the formula $C_{21}H_{23}O_4N$, whilst Scholtz (Arch Pharm. 1913, 251, 136) prefers the formula $C_{18}H_{21}O_3N$. F. L.-P.

BECKELITE. A silicate of calcium and cerium-earths $Ca_3(Ce,La,Di,Y)_4(Si,Zr)_3O_{15}$, containing Ce_2O_3 28·1, La_2O_3 13·6, Di_2O_3 18·0, $(Y,Er)_2O_3$ 2·8, ZrO_2 2·5 p.c., etc. It occurs as wax-yellow grains and cubic crystals as an accessory constituent in a dyke rock associated with elaeolite-syenite in the Mariupol district on the Sea of Azov, South Russia. The crystals (½ cm. diameter) have the form of octahedra and rhombic-dodecahedra, and resemble pyrochlore in general appearance and physical characters, but they possess a cubic instead of an octahedral cleavage. Chemically, however, they are quite distinct from pyrochlore, containing no columbium, titanium, or fluorine. Sp.gr. 4·15; hardness 5. L. J. S.

BEECHNUT OIL. This oil is derived from the seed-kernels of the beech tree (*Fagus sylvatica*, L.), which contain from 30 to 42 p.c., the yield from the whole nuts being from 10 to 12 p.c. The oil derived from the nuts of the Japanese beech (var. *Sieboldi*, Maxim.) is used for food and as a lubricant, for which latter purpose it is not well suited, as it is a 'semi-drying' oil. The cold-drawn oil is pale yellow, and has a pleasant odour and taste. It has sp.gr. 0·9205 at 15°; iodine value 111–120; and m.p. of fatty acids 17°–17·5° (Higuchi, Bull. Forest Exp. Stat. Tokyo, 1915). In Europe beechnut oil is sometimes used to adulterate almond oil.

C. A. M.

BEECH TAR. According to Fisher, 100 parts of beech wood yield on dry distillation 45 parts of acetic acid, 23 parts of charcoal, 4 of oil, and 28 of gas, consisting of 20 parts carbon dioxide, 7 of carbon monoxide, 0·5 of marsh gas, 0·05 of hydrogen, and 0·45 of water (Dingl. poly. J. 238, 55).

The tar contains phenol, cresol, phlorol, guaiacol, and creosol, the dimethyl ether of propyl pyrogallol, the dimethyl ether of pyrogallol, which on oxidation yield cœrulignone or cediret, pittacal, and picamar.

According to Gratzel (J. Pharm. [5] 6, 520), ferric chloride colours beech tar creosote a blue passing to brown.

(For a history of the investigations made upon wood tars, *v.* Schorlemmer, J. Soc. Chem. Ind. 4, 152, where also will be found a bibliography of the subject; *v.* also CREOSOTE, and WOOD, DESTRUCTIVE DISTILLATION OF.)

BEESWAX *v.* WAXES.

BEET-ROOT. The root of *Beta vulgaris* (Linn.). Many varieties are known, differing in colour, shape, and size. Mangel-wurzel, or mangold, as it is often called, is a variety (of which there are many sub-varieties), largely grown as winter food for cattle; garden beet-root, employed as salad or vegetable, is often understood when the term 'beet-root' is used. The most important variety, however, is the sugar beet, of which many sub-varieties are known. These have been obtained by careful selection with a view to obtaining the highest proportion of cane sugar.

The presence of sugar in the juice of beet-root was observed in 1747 by Marggraf, who suggested its extraction on a commercial scale. The early attempts, however, proved failures, as the process could not compete with the cane-sugar industry. This is not surprising when it is remembered that the beets then grown only yielded about 2 p.c. of sugar.

Careful selection of seed, and improved cultivation and methods of extraction, aided by a system of bounties by continental Governments, have resulted in beet sugar almost entirely replacing cane sugar in the principal markets of Europe (*v.* SUGAR).

Beet-root contains water, nitrogenous matters (including true albuminoids and the bases glutamine, betaine, and choline), pectins, sugars (of which cane sugar and raffinose are the chief), colouring matter of an unstable character (Formanek, J. pr. Chem. 1900, ii. 62, 310), and ash. It will be well to consider, in turn, the composition of average specimens of the three principal varieties of beet-root mentioned above.

(*a*) *Mangel-wurzel*, or *Mangolds*, called sometimes field beets. Many varieties, differing in colour, size, and shape, are in cultivation. They may be classified into long, tankard, and globe forms.

Mangolds grow best in deep, somewhat clayey soils, and in warm, fairly dry climates. They demand abundant supplies of plant food, and, under favourable conditions, yield very heavy crops, from 20 to 30 tons per acre being usually obtained. They are better as food for cattle and sheep after they have been stored for some weeks.

As in almost all root crops, large mangolds are distinctly more watery than small ones.

The following is the average composition of mangolds, according to (1) Warington, (2) Kellner :—

—	1		2		
	Large	Small	Large	Medium	Small
Water . .	89·0	87·0	89·5	88·0	86·5
Nitrogenous substances	1·2	1·0	1·3	1·2	1·1
Ether extract	0·1	0·1	0·1	0·1	0·1
Soluble carbohydrates	7·7	10·2	6·7	8·7	10·6
Crude fibre .	1·0	0·8	1·0	0·9	0·8
Ash . .	1·0	0·9	1·4	1·1	0·9
	100·0	100·0	100·0	100·0	100·0

The nitrogenous substances comprise real albuminoids, in proportion varying from 33 to 60 p.c. of the whole (being lowest in the large and highest in the small roots), and amides. Quite considerable quantities of nitrates are often present in the juice.

The soluble 'carbohydrates' consist chiefly of sugars, pectins, cellulose, and pentosans; starch is not present. The ash of mangolds, according to Wolff, contains:

K_2O	Na_2O	MgO	CaO	P_2O_5	SO_3	Cl	SiO_2
53·1	14·3	5·1	4·6	9·6	3·3	6·6	3·3

The unusually large proportion of chlorine is a noticeable feature. Beets, being descendants of a maritime plant, are found to be benefited by applications of common salt to the soil in which they are grown. Oxalic acid, to the extent of about 0·1 p.c., is present in beet-root.

(*b*) *Garden beet-root.* These are almost always red-fleshed. In composition they resemble the mangel-wurzel.

The average of 17 American analyses shows: Water, 87·6 p.c.; nitrogenous substances, 1·6 p.c.; fat, 0·1 p.c.; soluble carbohydrates and fibre, 9·6 p.c.; ash, 1·1 p.c.

(*c*) *Sugar beets.* Of these, many varieties have been obtained by careful selection. They are usually white- or yellow-fleshed, conical in shape, and grow with the root entirely underground. The sugar content now ranges from 10 or 11 to 16, 18, or even 20 p.c.

Roots not exceeding 1½ to 2 lbs. in weight are preferred. A deep medium loam containing a fair proportion of lime is the soil best suited for their growth. Nitrogenous manuring must be only sparingly done, or the roots become watery and deficient in sugar.

It is difficult to give the typical composition of sugar beets, since their sugar content varies so greatly with variety of plant, season, size of root, cultivation, and manuring. Small roots are almost invariably richer than large ones, other things being equal; a dry period during the ripening and maturing of the roots is also favourable to sugar formation; well-tilled soil, regularity of shape of root, and suitable manuring, are all important factors in determining the yield of sugar.

There is evidence that the careful selection of beets for sugar production has altered the plant considerably, so far as content of ash is concerned (Schneidewind, Bied. Zentr. 1900, 29, 81). The proportion of ash is much lower than formerly, the quantity of potash is only about half of what it was, while the soda has doubled; magnesia has remained unchanged, while phosphoric acid is less.

According to Kellner, the average composition of sugar beets is: Water, 75 p.c.; crude protein, 1·3 p.c.; fat, 0·1 p.c.; soluble carbohydrates, 21·4 p.c.; fibre, 1·5 p.c.; ash, 0·7 p.c. In addition to the sugar content, the purity coefficient (the ratio of cane sugar to total sugar) is of importance (*see* SUGAR).

The leaves of mangolds and sugar beets contain much oxalic acid, up to 8 p.c. of the dry matter (Stoklasa, Bied. Zentr. 1901, 30, 393), and their ash is rich in lime, magnesia, and soda. They contain about 84 p.c. water, 2·3 p.c. nitrogenous matter, 0·4 p.c. ether extract, 7·4 p.c. soluble carbohydrates, 1·6 p.c. fibre, and 4·8 p.c. ash.

They are sometimes used as cattle food, either in the fresh or dried condition, or sometimes as silage. In order to prevent ill effects from the oxalic acid present, it is recommended to sprinkle powdered calcium carbonate on the leaves before giving them to animals. About 1 lb. calcium carbonate to 1000 lbs. of leaves is sufficient (Kellner). The leaves are sometimes dried by artificial heat, and then furnish a valuable food, equal to meadow hay. H. I.

BEET-ROOT GUM *v.* GUMS.

BEHENIC ACID $C_{22}H_{44}O_2$ is said to be present as a glyceride in ben oil (*q.v.*). The fatty acid prepared from the oil melted at 80°–82° and solidified at 76° 79° (J. pr. Chem. 1894, 61). The acid prepared synthetically from erucic acid has m.p. 83°-84°, and solidifies at 77°-79°; b.p. (60 mm.) 306° (Talanzeff, J. pr. Chem. 1895, 50, 71). It forms acicular crystals, soluble in alcohol (0·102 p.c. at 17°) and ether (0·1922 p.c. at 16°); m.p. of ethyl ester, 48°-49°. A method of detecting rape oil in olive oil has been based on the hydrogenation of the liquid fatty acids, and separation of the behenic acid formed from the erucic acid (Biazzo and Vigdorcik, Annali Chim. Appl. 1916, 6, 185). C. A. M.

BELLADONNA. (Fr. *Belledame.*) The *Atropa belladonna* (Linn.), or deadly nightshade. A poisonous plant of the *Solanaceæ* order. Employed in medicine as an anodyne, &c., and for dilating the pupil. The name appears to have been derived from the circumstance of its employment in an Italian cosmetic. Its physiological action is due to *atropine.*

BELLITE. An explosive prepared by mixing a nitrate with a nitro-compound such as dinitrobenzene, trinitronaphthalene, or nitrotoluene, and then subjecting the mixture to a temperature of from 50° to 100° (Eng. Pat. 13690, Nov. 10, 1885; *v.* EXPLOSIVES).

BELLITE. This name has also been used (W. F. Petterd, 1905) for an incompletely determined mineral, described as a chromo-arsenate of lead, and occurring as bright-red or yellow velvety tufts, or as powdery encrustations, at Magnet in Tasmania. L. J. S.

BELL-METAL. An alloy of copper and tin used in the manufacture of bells. Contains from 3 to 4 parts of copper to 1 part of tin.

BELL-METAL ORE *v.* STANNITE.

BENGALINE *v.* AZO- COLOURING MATTERS.

BENGAL LIGHTS. These fires may be made by mixing potassium chlorate, carbon, antimony sulphide, strontium nitrate, &c., together in suitable proportions; but all such mixtures of potassium chlorate and sulphur are dangerous from their tendency to inflame spontaneously owing to sulphur frequently containing sulphuric acid. Saunders suggests that 120 grains of potassium bicarbonate should be added to each pound of sulphur to neutralise the free acid.

An improvement in the manufacture of Bengal lights has been suggested by Chertier (Wagner's Jahr. 24, 464), who obtains a smokeless and odourless fire by melting shellac and adding, with continuous stirring, the nitrate. The proportions given are: for red fires, one part of shellac to five of strontium nitrate; for green, one of shellac to five of barium nitrate; and for yellow, one of shellac to three of sodium nitrate. They burn slowly, and are well adapted for theatres, &c.

C. Schmidt has patented (D. R. P. 34020, 1885) the following process. From 1 to 10 grams of magnesium dust are added to 100 grams of collodion, and 3 grams of barium or strontium chloride are added. On evaporation of the ether, thin plates are obtained which burn with great brilliancy.

Another formula recommended by a German firm is, for white fires, to fuse one part shellac with six barium nitrate, grind and mix with 2·5 parts magnesium powder. For red fires, five parts strontium nitrate is used instead of the barium nitrate. These mixtures can be made into ribbons or charged into thin zinc tubes so as to make torches (Dingl. poly. J. 256, 518). (*See* also FLASH LIGHTS; PYROTECHNY.)

BENITOITE. This interesting mineral is an acid titano-silicate of barium $BaTiSi_3O_9$, and forms beautiful sapphire-blue, transparent crystals suitable for cutting as gems. The crystals afford the only known example (except Ag_2HPO_4 (H. Dufet, 1886)) of the ditrigonal-bipyramidal class. Sp.gr. 3·64–3·67; H. 6½. The dichroism is intense, the ordinary ray being colourless, and the extraordinary ray greenish-blue to indigo-blue. The mineral was first found (and described by G. D. Louderback) in 1907, near the source of the San Benito river in San Benito Co., California, the crystals occurring embedded in natrolite veins traversing schistose rocks. L. J. S.

BENJAMIN, GUM, *v.* BALSAMS.

BEN OIL, Behen Oil, is obtained from the seeds of the *Ben nut,* from *Moringa pterygosperma* (*oleifera*) and *Moringa aptera* (Gärt.).

The Moringa trees are indigenous to India, Arabia, and Syria, and were introduced to Jamaica from the East Indies in 1784. *Moringa pterygosperma* has also been found in Northern Nigeria and Dahomey. Ben oil has a slightly yellowish colour, is odourless, and has a sweetish taste. The oil consists of the glycerides of oleic, palmitic, and stearic acids; it also contains a solid acid of high melting-point, which, according to Völcker (Annalen, 64, 342), is identical with behenic acid (m.p. 76°); though possibly this acid may be arachidic acid. In the East, ben oil is used for cosmetic purposes, it is also employed in the 'maceration' process for extracting perfumes from flowers. In the West Indies the oil is used for edible purposes. Jamaica oil, from which any solid deposit has been separated by filtration, is used for lubricating watches and other delicate machinery, for which purpose it is particularly suitable owing to its not readily oxidising when exposed to the air. This property is in accordance with the low iodine value of the oil. A genuine sample from Jamaica, examined by Lewkowitsch (Analyst, 1903, 28, 343) gave the following results: sp.gr. at 15°, 0·9127; iodine value, 72·2; iodine value of liquid fatty acids, 97·53; and butyro-refractometer reading, 50·0°. The low iodine value of the liquid fatty acids indicates that fatty acids more unsaturated than oleic acid were only present in small proportion. Commercial samples of ben oil frequently have much higher iodine values (*e.g.* 110), but the genuine character of these is open to question. J. L.

BENZACETIN *v.* SYNTHETIC DRUGS.

BENZAL CHLORIDE. *Benzylidene chloride, Benzidene chloride* (*v.* TOLUENE, CHLORINE DERIVATIVES OF).

BENZALDEHYDE C_7H_6O or $C_6H_5{\cdot}CHO$. *Benzoic aldehyde, Benzoyl hydride. Ethereal,* or *volatile,* or *essential oil of bitter almonds. Essence of bitter almonds.* (*Aldehyde benzoïque,* Fr.; *Bittermandelöl,* Ger.) Mortrès showed, in 1803, that, in addition to the fatty oil, a volatile oil could be obtained from bitter almonds; but pure benzaldehyde was first isolated, its composition determined, and its reactions studied, by Liebig and Wöhler in 1837 (Annalen, 22, 1). Benzaldehyde is not contained, as such, in bitter almonds: it is produced by the action of a soluble ferment, *emulsin* (also termed *synaptase*), present in the almond, on *amygdalin* $C_{20}H_{27}NO_{11}$. In this fermentation, which occurs when the bruised almonds are mixed with cold water, the amygdalin is hydrolysed, yielding benzaldehyde, together with hydrocyanic acid and glucose:

$$C_{20}H_{27}NO_{11}+2H_2O=C_7H_6O+HCN+2C_6H_{12}O_6$$

If boiling water is used, the ferment is destroyed and the reaction does not take place. Peach kernels and kernels of other stone fruits containing amygdalin also yield benzaldehyde. It occurs, ready formed, in the leaves of the cherry laurel (*Prunus laurocerasus*), of the bird cherry (*Prunus padus*), and of the peach (*Amygdalus persica*).

Preparation.—1. *From bitter almonds.* The bitter almonds (or more rarely, peach kernels) are ground and then cold-pressed, to extract the fatty oil. The press cake is made into a thin cream with cold water, introduced into a still, allowed to stand for 24 hours, and then distilled either by blowing in superheated steam, or, less advantageously, over a fire, in which case mechanical stirring must be employed to prevent the charring of the vegetable matter. The distillation is continued as long as the distillate appears milky. Most of the crude benzaldehyde separates as an oily layer under the aqueous distillate; some, however, remains in solution and may be recovered by distilling the aqueous liquid, when the benzaldehyde passes over with the earlier portions.

Michael Pettenkofer (Annalen, 122, 77) modifies the foregoing process as follows:—12 parts of the coarsely powdered press cake are added to 100–120 parts of boiling water, stirring during the process, and the mixture is kept boiling for about half an hour. In this way all the amygdalin is obtained in solution. The liquid is then allowed to cool; 1 part of ground bitter almonds, suspended in 6–7 parts of cold water, is added, and after standing for 12 hours the whole is slowly distilled. According to Pettenkofer, the maximum yield of benzaldehyde is thus obtained, no amygdalin remaining undecomposed. Pelz, however, states (J. 1864, 654) that the yield of benzaldehyde in this process is no greater than is obtained by macerating merely the above-mentioned 1 part of ground bitter almonds with cold water and then distilling.

The oil prepared by either of these methods contains hydrocyanic acid, from which it may be freed by fractional distillation, the hydrocyanic acid coming over with the first part of the distillate. The hydrocyanic acid may also be removed without distillation by shaking the oil with a mixture of milk of lime and ferrous sulphate (Liebig and Wöhler). The purest benzaldehyde is obtained by shaking the crude product with 3–4 times its volume of a concentrated solution of sodium bisulphite, washing the crystals of the double compound

$$(C_7H_6O,NaHSO_3)_2H_2O$$

with alcohol, recrystallising them from water, and distilling them with a solution of sodium carbonate (Bertagnini, Annalen, 85, 183; Müller and Limpricht, *ibid.* 111, 136).

2. *From toluene.*—At the present day benzaldehyde is generally prepared artificially from chlorinated derivatives of toluene. The following are the chief processes that have been proposed:—

Lauth and Grimaux (Bull. Soc. chim. [2] 7, 105) boil 1 part of benzyl chloride $C_6H_5{\cdot}CH_2Cl$, 1½ parts of lead nitrate (or copper nitrate), and 10 parts of water with a reflux condenser for several hours, passing a current of carbon dioxide through the apparatus to prevent oxidation. Half the liquid is then distilled off, and the oil, which separates in the distillate, is rectified. The product, which consists mainly of benzaldehyde, may be further purified by converting it into the bisulphite compound.

The Dow Chemical Co. (U.S. Pat. 1272522) heat benzyl bromide with an aqueous solution of calcium nitrate or sodium nitrate. The reaction takes place between equimolecular proportions of benzyl bromide and sodium nitrate, and the benzaldehyde is practically a pure product.

H. Schmidt (D. R. P. 20909; J. Soc. Chem.

Ind. 1883, 274) chlorinates boiling toluene until it attains a sp.gr. of 1·175, when it consists essentially of a mixture of 2 mols. of benzyl chloride with 1 mol. of benzal chloride. This product is boiled with six times its volume of water and a quantity of powdered black oxide of manganese containing two atoms of available oxygen to the above molecular proportion. The reaction is supposed to take place according to the equation

$$2C_6H_5{\cdot}CH_2Cl + C_6H_5{\cdot}CHCl_2 + 2MnO_2$$
$$= 3C_6H_5{\cdot}CHO + 2MnCl_2 + H_2O$$

The product is steam-distilled, and the aldehyde purified in the usual way. A mixture of benzyl bromide and benzal bromide may be substituted for the chlorine compounds.

Another method consists in heating benzal chloride with milk of lime under pressure.

$$C_6H_5{\cdot}CHCl_2 + Ca(OH)_2 = C_6H_5{\cdot}CHO + CaCl_2 + H_2O$$

According to Espenschied (D. R. P. 47187), the reaction takes place under ordinary pressures if insoluble substances such as chalk or barium sulphate are added along with the milk of lime, so as to produce an emulsion of the benzal chloride.

E. Jacobsen (D. R. P. 11494 and 13127; Ber. 13, 2013, and 14, 1425) heats benzal chloride with an organic acid (or an ethereal salt of an organic acid) and a metallic chloride, oxide, or sulphide. Thus benzal chloride, when heated on the water-bath with acetic acid and a little zinc chloride, yields benzaldehyde, acetyl chloride, and hydrochloric acid.

$$C_6H_5{\cdot}CHCl_2 + CH_3{\cdot}CO_2H = C_6H_5{\cdot}CHO + CH_3{\cdot}COCl + HCl$$

The acetyl chloride, owing to its much lower boiling-point, may be readily removed from the benzaldehyde by distillation.

Benzaldehyde can be prepared by oxidising benzyl aniline to benzylidene aniline, which, on addition of acids, splits into benzaldehyde and aniline. For this purpose 100 kilos. of benzyl aniline, and from 500–1000 litres of water are placed in a large retort fitted with an agitator; during agitation and boiling the following mixture is gradually run in during a few hours: potassium or sodium bichromate, 50 kilos; water, 200 litres, acidulated with hydrochloric acid (20°B.), 165 kilos, or its equivalent of sulphuric acid; distillation ensues, water and benzaldehyde coming over. The nitrobenzaldehydes may be obtained by substituting the corresponding nitrobenzylaniline. Another method consists in oxidising the salt of the benzylaniline sulphonic acid to the benzylidene compound, and then treating it with the salt of an aromatic base, followed by hydrochloric acid. The aldehyde is formed, and the aromatic base can be recovered and used for another operation (Farb. vorm. Meister, Lucius, and Brüning, Eng. Pat. 10689 and 30118; D. R. P. 110173; J. Soc. Chem. Ind. 1897, 558, and 1899, 36). It has been prepared by passing a current of air charged with the vapour of toluene through a chamber containing a catalyser such as oxide of iron, and heated between 150° and 300°. By substituting porous carbon for oxide of iron and using a higher temperature, benzoic acid may be obtained (Chavy, Delage, and Woog, Fr. Pat. 379715; J. Soc. Chem. Ind. 1907, 1254, Ipatieff, Ber. 1908, 993).

It has also been prepared by the oxidation of benzyl aniline, or benzyl toluidine with chromic acid mixture or with potassium permanganate solution in acetone (D. R. PP. 91503, 92084; Frdl. iv. 129, 131).

It has also been prepared from phenyl magnesium bromide and orthoformic ester (Farb. vorm. Fried. Bayer & Co. D. R. P. 157573; Chem. Zentr. 1905, i. 309). By using 15 grams of magnesium, 100 grams of bromobenzene, and 60 grams of orthoformic ester, a 90 p.c. yield can be obtained (Bodroux, Compt. rend. 1904, i. 92). Gatterman's adaptation of the Friedel and Crafts reaction (Annalen, 1906, 347, 347) has also been employed for the preparation of benzaldehyde. In this process benzene is condensed with hydrogen chloride and carbon monoxide in the presence of aluminium chloride and cuprous chloride, the mixture of gases acting potentially as formyl chloride; condensation following the usual course (D. R. P. 126421)

$$C_6H_6 + Cl{\cdot}CHO = C_6H_5{\cdot}CHO + HCl$$

Schulze (D. R. PP. 82927, 85493) heats benzotrichloride at 25°–30° with some ferric benzoate or finely divided iron, water is then added, and the mixture warmed to 90°–95°, when hydrochloric acid distils over. The residue is decomposed by milk of lime and distilled in a current of steam to obtain the aldehyde.

Owing to the fact that the product obtained from the chlorinated derivatives of toluene frequently contains chloro- compounds, methods have been devised for the direct oxidation of toluene to the aldehyde. Raschig (Chem. Zeit. 1900, 24, 446) uses manganese dioxide in the presence of 65 p.c. sulphuric acid at 40°. 300 kilos of toluene are mixed with 700 kilos sulphuric acid, and 90 kilos finely powdered precipitated manganese dioxide are added, the whole being violently shaken during the addition, and the temperature kept at 40°. After completion of the action the benzaldehyde and unaltered toluene are driven over and the aldehyde separated in the usual manner (*cf.* D. R. PP. 101221, 107722). The Badische Anilin u. Soda-Fabrik use nickel and cobalt oxides, as oxidants (D. R. P. 127388), whilst the firm of Meister, Lucius, und Brüning (D. R. P. 158609) have suggested the use of cerium compounds.

By passing a stream of carbon monoxide and hydrochloric acid gas (2 : 1) through a cooled mixture consisting of equal weights of aluminium bromide and benzene, and $\frac{1}{10}$ their weight of copper chloride, a solid mass is obtained: this is decomposed by ice water, extracted with ether, and fractionated. The yield is 85–90 p.c. (Reformatsky, D. R. P. 126421; Chem. Zentr. 1901, i. 1226; ii. 1372).

Benzaldehyde has also been prepared by the electrolytic reduction of benzoic acid or its salts. An electrode of finely divided graphite and benzoic acid is employed as the cathode of the cell, the anode being of lead or platinum. The solution in the cell is 20 p.c. sulphuric acid, saturated with benzoic acid, the current used is 1·5 amp. per sq. dcm., and 12–15 volts (Mithack, D. R. P. 123554; Chem. Soc. Abstr. 1902, i. 291). Mettler (Ber. 1908, 4148) uses a sodium-amalgam electrode; and Moest (D. R. P.

138442; Chem. Zentr. 1903, i. 370) electrolyses a solution of sodium phenylacetate.

A method has been described for purifying benzaldehyde by dissolving it in sulphurous acid and precipitating the bisulphite compound by adding potassium chloride (Chem. Fab. Griesheim-Elektron, D. R. P. 154499; Chem. Zentr. 1904, ii. 965).

Other modes of formation.—Benzaldehyde is also formed in the following reactions, which, however, are not of practical importance. By distilling a mixture of calcium benzoate and calcium formate (Piria, Annalen, 100, 105); by the oxidation of benzyl alcohol (Cannizzaro, Ann. Chim. Phys. [3] 40, 234); of cinnamic acid (Dumas and Peligot, Annalen, 14, 50; Harries, Ber. 1903, 1296); or of stilbene (Harries, *l.c.*); by the reduction of benzoic acid, either with sodium amalgam in acid solution (Kolbe, Annalen, 118, 122), or by passing its vapour over heated zinc-dust (Baeyer, Annalen, 140, 296); by treating toluene with chromyl chloride and then with water (Étard, Ann. Chim. Phys. [5] 22, 225); by treating 1 molecule of benzal chloride with slightly more than 2 molecules of acetic acid (Béhal, Compt. rend. 148, 179); by acting on benzophenoneoxime with phosphorus pentasulphide, and decomposing the thiobenzanilide thus formed with boiling alkali and zinc-dust (Cuisa, Chem. Zentr. 1907, i. 28).

Properties.—Benzaldehyde is a colourless, strongly refractive liquid with a pleasant aromatic odour, boiling at 179°–180°, and solidifying at −13·5° (Pictet, Compt. rend. 119, 955; Altschul and Schneider, Zeitsch. physical. Chem. 1895, 24); sp gr. 1·0504 15°/4° (Mendeléeff, J. 1860, 7). It is soluble in 300 parts of water, and miscible in all proportions with alcohol and ether. It is non-poisonous, the poisonous properties of ordinary oil of bitter almonds being due to the presence of hydrocyanic acid. Its magnetic rotatory power has been studied by Perkin (J. Chem. Soc. 1896, 1064).

Reactions.—Benzaldehyde readily undergoes oxidation; thus it absorbs oxygen from the air, forming benzoic acid. The presence of hydrocyanic acid protects it from oxidation; according to Dusart (Bull. Soc. chim. 8, 459), it is therefore usual to add hydrocyanic acid to artificial benzaldehyde. Taken internally, benzaldehyde is oxidised in the organism, reappearing in the urine as hippuric acid and benzamide. Aqueous *caustic potash* converts it into benzoic acid and benzyl alcohol

$$2C_6H_5{\cdot}CHO+KOH=C_6H_5{\cdot}CO_2K+C_6H_5{\cdot}CH_2OH$$

When warmed with alcoholic potassium cyanide it is converted into benzoin

$$C_6H_5{\cdot}CHOH{\cdot}CO{\cdot}C_6H_5$$

It forms crystalline compounds with the *bisulphites of the alkali metals*; thus:

$$(C_7H_6O,NaHSO_3)_2H_2O$$

Under the influence of dehydrating agents, it readily undergoes condensation with various other substances; thus when heated with *acetic anhydride and dry sodium acetate* it yields cinnamic acid.

$$C_6H_5{\cdot}CHO+CH_3{\cdot}CO_2H=C_6H_5{\cdot}CH:CH{\cdot}CO_2H+H_2O$$

(Perkin, J. Chem. Soc. 31, 389); cinnamic acid is also obtained from *ethyl acetate* and benzaldehyde (Claisen, Ber. 1890, 976; Farb. vorm. Meister, Lucius and Brüning, D. R. P. 53671; Ber. 1891, Ref. 180). It combines with hydrazine to form benzalazine $C_{14}H_{12}N_2$, which, on distillation, yields stilbene (diphenyl-ethylene) $C_6H_5{\cdot}CH:CH{\cdot}C_6H_5$. With *dimethylaniline* in presence of zinc chloride it forms the compound $C_6H_5{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$, the leuco- base of benzaldehyde green which, by oxidation, is converted into that colouring matter (O. Fischer, Ber. 11, 950).

When hydrogenated in presence of nickel between 210° and 235°, benzaldehyde yields a mixture of benzene and toluene, together with their hexahydrides. Under other conditions it may be reduced by the catalytic action of metals and hydrogen to benzyl alcohol.

With pyrogallol benzaldehyde forms dyestuffs of the triphenylmethane series (Hofmann, Ber. 1893, 1139), and with chloracetopyrogallol a golden-yellow dyestuff (Kusselkaul and Kostanecki, Ber. 1896, 1886). By heating benzaldehyde with a little sulphur in a sealed tube, stilbene and benzoic acid are formed (Barbaglia and Marquardt, Ber. 1891, 1881).

Derivatives.—The most important derivatives are the sulphonic acids, which are the parent substances of various dyestuffs (Gnehm and Schüle, Annalen, 299, 347). Benzaldehyde *o*-sulphonic acid (Kafa, Ber. 1891, 791; Wallach and Wüster, Ber. 1893, 150; Gnehm and Schüle, Annalen, 1898, 24; D. R. P. 88952), Benzaldehyde *p*-sulphonic acid (Farb. vorm. Sandoz, D. R. P. 151528; Chem. Zentr. 1904, ii. 1269).

Impurities and adulterations.—Benzaldehyde very frequently contains hydrocyanic acid, either originally present or subsequently added (*v. supra*), and benzoic acid, formed by spontaneous oxidation. The artificial product generally contains chlorinated benzaldehydes. Alcohol, ethereal oils, and nitrobenzene are sometimes fraudulently added: the latter substance resembles benzaldehyde in smell.

In order to test the purity of a sample of benzaldehyde, the sp.gr. and boiling-point should first be determined, as both of these are altered by the presence of impurities. The substance should also dissolve without residue in a solution of sodium bisulphite.

Of the impurities above mentioned, hydrocyanic acid may be detected by distilling the oil and then testing the first portions of the distillate by the Prussian-blue test; chlorine compounds, by heating the oil with metallic sodium, when sodium chloride will be formed, in which the chlorine can be detected by silver nitrate, taking care, however, to distinguish between silver chloride and silver cyanide, as this latter will be formed if hydrocyanic acid or nitrobenzene is present; alcohol, by the iodoform test; and ethereal oils or nitrobenzene, by dissolving the sample in sodium bisulphite, when these admixtures remain behind. Bourgoin (Ber. 5, 293) tests for nitrobenzene in benzaldehyde by mixing the sample with twice its volume of caustic potash: if nitrobenzene is present, the mixture turns green, and on adding water the liquid forms two layers, of which the under layer is yellow and the upper green, this latter turning red on standing for some hours.

Estimation.—The reagent employed consists of 1 c.c. of freshly redistilled phenylhydrazine, 0·5 c.c. glacial acetic acid dissolved in 100 c.c. distilled water. The liquid containing the benzaldehyde is heated on the water-bath for half an hour, set aside for 12 hours, and filtered through a Gooch crucible, dried over conc. sulphuric acid, and weighed. Weight of phenyl hydrazone ×0·5481 gives the amount of benzaldehyde present. Small quantities may be satisfactorily estimated by this method (Hérissey, J. Pharm. 1906, 60; Dennis and Dunbar, J. Soc. Chem. Ind. 1099, 488). Another method consists in estimating benzaldehyde colorimetrically with fuchsin decolourised with sulphurous acid (Woodman and Lyford, J. Amer. Chem. Soc. 1908, 1607).

To estimate the presence of benzoic acid, 50 c.c. of the sample are shaken with water and 10 c.c. N-sodium hydroxide, the excess alkali being then back titrated with N-acid, using phenolphthalein as indicator.

SUBSTITUTION DERIVATIVES OF BENZALDEHYDE.

o-**Nitrobenzaldehyde.** It may be prepared by the oxidation of the dimercury derivative of *o*-toluene (Reissert, D. R. P. 186881; Chem. Soc. Abstr. 1907, i. 1046; Kalle & Co., D. R. P. 199147; Chem. Soc. Abstr. 1909, i. 76); by the oxidation of *o*-nitrotoluene with manganese dioxide or by passing the vapour of the hydrocarbon over manganese dioxide heated to 210°–250° (Gilliard, Monnet and Cartier, D. R. P. 101221; Chem. Zentr. 1899, i. 960; Bad. Anil. u. Sod. Fab., Eng. Pat. 21947; J. Soc. Chem Ind. 1900, 892); by the oxidation of *o*-nitrotoluene with nickel oxide, nickel chloride, and hypochlorite (Bad. Anil. u. Sod. Fab., D. R. P. 127388; Chem. Zentr. 1902, i. 150); by the oxidation of *o*-nitrobenzylaniline (*q.v.* benzaldehyde); by the oxidation of *o*-nitrobenzylalcohol and its esters (Eug. Fischer, D. R. P. 48722; Frdl. ii. 98; Kalle & Co., D. R. PP. 104360, 106712; Chem. Zentr. 1899, ii. 950; 1900, i. 885); by the hydrolysis of *o*-nitrobenzaldehyde diacetate, which is obtained by the oxidation of *o*-nitrotoluene with a mixture of acetic anhydride, acetic acid, and sulphuric acid (Thiele and Winter, Annalen, 311, 356; Fried. Bayer & Co., D. R. P. 121788; Chem. Zentr. 1901, ii. 70); or by the oxidation of the sodium salt of *o*-nitrophenylnitromethane by potassium permanganate at low temperature in aqueous solution (Soc. Chim. des Usines du Rhône, D. R. P. 237358)

$$3C_6H_4(NO_2)CH : NOONa+2KMnO_4+H_2O$$
$$=3C_6H_4(NO_2)CHO+3NaNO_2+2MnO_2+2KHO$$

Properties.—Large yellow needles, m.p. 46°. When treated with acetone and caustic soda it yields indigotin (Baeyer, Ber. 15, 2856). With methyl- and ethyl-aniline or their sulphonic acids it condenses to form leuco-bases of blue-green triphenyl methane dyestuffs (Clayton Aniline Co., D. R. P. 108317; Chem. Zentr. 1900, i. 1081).

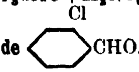
m-**Nitrobenzaldehyde.** It may be prepared by dissolving 1 volume of benzaldehyde in a mixture of 5 volumes of fuming nitric acid, and 10 volumes of sulphuric acid, precipitating by addition of water and recrystallising from dilute alcohol (Widmann, Ber. 13, 678; Bertagnini, Annalen, 79, 260).

Properties.—Pale-yellow needles, m.p. 58°. It condenses with the sulphonic acids of the tertiary aniline bases to yield dyestuffs (Kalle & Co., D. R. P. 73147, Frdl; iii. 85).

p-**Nitrobenzaldehyde.** It is prepared by similar methods to those by which the ortho-compound is obtained (D. R. PP. 91503, 92084, 93539; Frdl. iv. 129); by heating *p*-nitrobenzylalcohol with copper oxide or other metallic oxides (Schmidt, D. R. P. 15881; Frdl. i. 60).

Properties.—Colourless prisms, m.p. 106°. It condenses with benzene and its homologues by addition of sulphuric acid to form *p*-nitrotriphenylmethane (Stolz, D. R. P. 40340; Frdl. i. 58); with secondary and tertiary amines to form alkyl- and aryl- derivatives of *p*-nitrodiaminotriphenylmethane (O. Fischer, D. R. PP. 16766, 16707; Frdl. i. 54); and with the sulphonic acids of tertiary aniline bases (Kalle & Co., D. R. P. 73147; Frdl. iii. 86). The sulphonic acid of *p*-nitrobenzaldehyde is prepared by the oxidation of *p*-nitrotoluene *o*-sulphonic acid, and from it blue and bluish-red dyestuffs of the triphenylmethane series are easily obtainable (Green and Wahl, Eng. Pat. 21825; J. Soc. Chem. Ind. 1898, 915). 2.4-**Dinitrobenzaldehyde** has been prepared by Sachs (Ber. 1902, 35, 1228) by condensing 2·4-dinitrotoluene with *p*-nitrosodimethylaniline and decomposition of the resultant product by acid

$$(NO_2)_2C_6H_3{\cdot}CH_3+NO{\cdot}C_6H_4{\cdot}N(CH_3)_2$$
$$=(NO_2)_2C_6H_3{\cdot}CH=NC_6H_4N(CH_3)_2$$
$$(NO_2)_2C_6H_3{\cdot}CH=NC_6H_4N(CH_3)_2+H_2O$$
$$=(NO_2)_2C_6H_3CHO+H_2NC_6H_4N(CH_3)_2$$

o-**Chlorbenzaldehyde**  It is prepared by the oxidation of *o*-chlortoluene with manganese dioxide and sulphuric acid (Gillard, Monnet et Cartier, D. R. P. 101221; Chem. Zentr. 1899, i. 960), by extraction from the products of the incomplete chlorination of *o*-nitrotoluene (Kalle & Co., D. R. PP. 110010, 115516; Chem. Zentr. 1900, ii. 460, 1168).

Properties.—It is a liquid, freezing at −4°, and boiling at 208° (748 mm.); sp.gr. 1·29 at 8°. By heating with sulphite it is converted into benzaldehyde *o*-sulphonic acid (Geigy & Co., D. R. P. 88952; Frdl. iv. 113). It is easily condensed with aromatic secondary and tertiary amines to yield dyestuffs of the triphenylmethane group (Geigy & Co., D. R. P. 94126; Chem. Zentr. 1898, i. 296). By sulphonation, 1 : 3 : 6-chlorbenzaldehyde sulphonic acid is produced, which when condensed with secondary or tertiary amines and then oxidised yields greenish-blue or blue dyestuffs (Soc. Chem. Ind. of Basle, Eng. Pat. 25128; J. Soc. Chem. Ind. 1897, 137; Gnehm and Schüle, Annalen, 299, 347).

m-**Chlorbenzaldehyde.** It is obtained from *m*-nitrobenzaldehyde by replacing the nitro-group by chlorine (Erdmann and Schwechten, Annalen, 260, 259; Eichengrün and Einhorn, *ibid.* 262, 135). It crystallises in prisms, m.p. 17°, and boils at 213°.

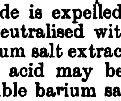
p-**Chlorbenzaldehyde.** It is associated with the ortho- compound in most preparations, and may be obtained from the mixture by sulphonating the ortho- compound by treatment with fuming sulphuric acid (Gesel. f. Chem. Ind., D. R. P. 98229; Chem. Zentr. 1898, ii. 743); by nitrating the ortho- compound with nitric and sulphuric acids, and steam-distilling the para-compound (Gesel. f. Chem. Ind., D. R. P. 102745; Chem. Zentr. 1899, ii. 408); by fractional distillation (Farb. vorm. Meister, Lucius and Brüning, D. R. P. 207,157; J. Chem. Soc. Abst. 1909, i. 307). It is a crystalline solid, melting at 47·5°, and boiling at 213°–214°.

Of the **dichlorbenzaldehydes** the 2 : 5- and 2 : 6-dichlor- compounds are the parent substances of many dyestuffs 2 : 5-**dichlorbenzaldehyde** (Gnehm and Bänziger, Ber. 1896, 875; Schüle, Annalen, 299, 34) melts at 57°–58°, and is obtained by the action of antimony pentachloride on benzaldehyde in the presence of iodine. 2 : 6-**dichlorbenzaldehyde** (Anil. Fabw und Ext. Fabrik., D. R. P. 199943; Chem. Soc. Abstr. 1908, i. 986). Reduction of the nitrobenzaldehydes yields the amino-benzaldehydes, of which the most important is the para-compound. This may also be prepared by heating *p*-nitrotoluene with sulphur and sodium hydroxide (Geigy, D. R. P. 86874). Bayer & Co. (D. R. P. 218364) separate the amino-benzaldehydes by reducing the crude nitro- compounds with hot sodium hydrosulphite solution, cooling to 50°, and acidification with hydrochloric acid. The mixture is then boiled for one minute, and, on cooling, the anhydro-compound of the *o*-aminoaldehyde separates, whilst the *m*-aminobenzaldehyde remains in solution, and can be recovered, and hence used for the preparation of the *m*-hydroxybenzaldehyde. *p*-Dimethylamino benzaldehyde $(CH_3)_2N{\cdot}C_6H_4{\cdot}CHO$ is best obtained by Ullmann and Frey's method (Ber. 1904, 37, 859), in which *p*-dimethylaminobenzyl alcohol (from dimethylaniline and formaldehyde) is condensed with *p*-nitrosodimethylaniline, and the resulting compound decomposed by nitrous acid. It crystallises in colourless needles, melts at 73°, and is used in the preparation of triphenylmethane dyes.

Hydroxybenzaldehydes (*q.v.*) **Salicylaldehyde.**

BENZALDEHYDE GREEN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BENZALDEHYDE-*o*-SULPHONIC ACID



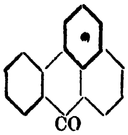
The most technically important member of the group, is obtained by heating *o*-chlorobenzenealdehyde with an aqueous solution of sodium sulphite under pressure at 170°–180°, and treating the product with sulphuric acid. When the sulphur dioxide is expelled by boiling, the cooled liquid is neutralised with sodium carbonate, and the sodium salt extracted with alcohol. Or the sulphonic acid may be converted into the sparingly soluble barium salt (Geigy & Co., D. R. P. 88952).

The free acid is a syrup; the sodium and barium salts crystallise in prisms (Gnehm and Schüle, Annalen, 1898, 299, 347).

The acid may also be prepared by oxidising stilbene disulphonic acid with potassium permanganate (Levinstein. Eng. Pat. 21968, 1897).

BENZAMIC ACID *v.* AMINO- ACIDS (aromatic).

BENZANTHRONE,



Prepared by heating a mixture of anthranol with sulphuric acid and glycerol at 120°, treating the product with water, washing the crude substance with sodium hydroxide solution, pressing, and drying. May be prepared from anthracene by treatment with sulphuric acid and glycerol (Badische Anilin und Soda Fabrik, D. R. P. 176019); and by condensing anthranol with acetin, or 2-aminoanthraquinone with dichlorohydrin (*idem.* D. R. P. 204354); or by heating phenyl-α-naphthyl ketone with aluminium chloride or ferric chloride. For other syntheses, *v.* Schaarschmidt and Korten, Ber. 1918, 51, 1074; Schaarschmidt and Georgeacopol, Ber. 1918, 51, 1082; *v.* KETONES.

Crystallised from alcohol benzanthrone forms pale yellow needles, m.p. 170°. Used in the manufacture of indanthrene dyes (*see* Benzanthrone Colours, art. INDANTHRENE).

BENZAURIN *v.* AURIN.

BENZENE AND ITS HOMOLOGUES.

Benzene. (*Benzol, Benzole*, Fr.; *Benzol*, Ger.) The name of this substance was derived in its original form from that of gum benzoïn, probably as *benzoïn oleum*, hence *benzole*, which latter form is still in use amongst nearly all distillers and users of it both in this country and on the Continent. In more strictly scientific literature, however, the name *benzene* has now become generally accepted, and the systematic termination *-ene* is employed in the names of its various homologues, as toluene, xylene, cymene, &c.

Pure benzene is a limpid, colourless, highly refracting liquid at ordinary temperatures. Its sp.gr. at 0° is 0·8991 (Kopp), 0·90023 (Adriaansz), and at 15° 0·8841 (Mendeléeff).

Its refraction index for the D line at 15·2° is 1·4957 (Adriaansz); at 9°, 1·4593 for A, 1·5050 for D, 1·5037 for H (Gladstone); at 8·5°, 1·50381 for H_α (Perkin, Chem. Soc. Trans. 1900, 77, 273).

When surrounded by ice it becomes solid, and if crystallisation is allowed to take place slowly, rhombic crystals are produced, the axes of which, *a, b, c*, are 0·891, 1, 0·799 (Groth). The solid melts at 5·483° (Richards and Shipley, J. Amer. Chem. Soc. 1914, 36, 1825).

It contracts on solidification, the difference in the specific volume of the liquid and solid $v_l - v_s = \Delta v$ is between 0·1219 and 0·1304 at 5·35° (Heydweiller, Ann. Phys. Chem. 1897, (iii.) 61, 527).

It exhibits no absorption lines or bands in the visible portion of the spectrum. Beyond H, however, photographs show a series of four bands covering the region lying between W.L. 3171 and 2190 tenth-metres. The methylated benzenes, toluene, and the three xylenes exhibit a similar absorption, requiring, indeed, very careful measurement to distinguish one from the other (Hartley, Chem. Soc. Trans. 1885, 47, 685; Proc. Roy. Soc. 1908, 80, A, 162; Hartley and Dobbie, Chem. Soc. Trans. 1898, 73, 695; Baly and Collie, *ibid.* 1905, 87, 1332; Friederichs, Zeitsch. photochem. 1905, 3, 154; Grebe, *ibid.* 376; Mies, *ibid.* 1909, 7, 357; 1910, 8, 287; Witte, *ibid.* 1915, 14, 347; Massol and Faucon, Compt. rend. 1918, 166, 819).

Benzene is an excellent solvent, easily dissolving caoutchouc and asphaltum, if they have not been exposed to light, though the protective effect of the light on the asphaltum is but slight, and prolonged treatment with benzene causes it to dissolve. Nearly all the gum resins, sulphur, phosphorus, fats, oils, most of the natural alkaloids, and many other organic compounds, are soluble in it. It has also, in common with carbon disulphide, the property of dissolving iodine with production of a violet solution.

Benzene is itself soluble to a very slight extent in water, considerably more so in alcohol, whilst ether, glacial acetic acid, acetone, and carbon disulphide, dissolve it readily.

Benzene boils under normal pressure at 80·36° (Regnault). For benzene from coal tar, Adriaansz found 80·53° to 80·62°; and for that obtained from benzoic acid prepared from gum benzoin, 80·60° to 80·67°; 80·2° (corr.) Thorpe and Rodger. Its specific heat at temperatures between $-185°$ and $+20°$ is 0·176 (Nordmeyer and Bernouilli, Ber. Deut. physikal. Ges. 1907, 5, 175) and at 94° is 0·4814 (Schlamp, Ann. Phys. Chem. 1896, (iii.) 58, 759). The latent heat of vaporisation is 94·37 (Griffiths and Marshall, Phil. Mag. 1896, (v.) 41, 1) or 94·93 (Campbell Brown, Chem. Soc. Trans. 1905, 87, 265).

For observations on its thermal expansion, *see* Kopp (Jahr. 1847–1848, 66), Louguinine (Ann. Chim. Phys. 4, 11, 465), Adriaansz (Bull. Soc. chim. 20, 1873).

The vapour when inhaled produces giddiness and ultimately insensibility.

Benzene forms with picric acid the molecular compound $C_6H_2(NO_2)_3OH,C_6H_6$, which melts with decomposition at 90°.

Oxidising agents, such as potassium permanganate or manganese dioxide and sulphuric acid, convert it into formic, propionic, and oxalic acids, together with small quantities of benzoic and phthalic acids, the latter substances being produced by the simultaneous oxidation of formic acid and benzene, the process of condensation resembling that occurring in the conversion of dimethylaniline into methyl violet. When strongly heated in sealed tubes or when passed slowly through strongly heated open tubes, condensation and decomposition go on together, acetylene, diphenyl, diphenylbenzene, &c., being formed with evolution of hydrogen and deposition of carbon (*cf.* Smith and Lewcock, Chem. Soc. Trans. 1912, 101, 1453; Zanetti and Egloff, J. Ind. Eng. Chem. 1917, 9, 350).

There can be little doubt that toluene and xylenes can also be produced in this way, and since Berthelot has shown that toluene and xylene when passed through strongly heated tubes can produce anthracene and naphthalene, and since he also obtained anthracene by so treating a mixture of benzene and ethylene, we may assume that if benzene is *not* the mother substance of the whole series of hydrocarbons obtained from coal tar, it is yet capable, under proper conditions, of generating all the others.

Vapour of benzene mixed with hydrogen passed over finely divided nickel heated to 170°–190° yields cyclohexane C_6H_{12}. The homologues of benzene behave similarly.

By passing dry ammonia through benzene containing calcium shavings a calcium-ammonia compound $Ca(NH_3)_4$ is formed, which with the benzene produces *dihydrobenzene* C_6H_8:

$$Ca(NH_3)_4=Ca(NH_2)_2+2N_2H+H_2$$
$$H_2+C_6H_6=C_6H_8$$

(Dumanski and Zvereva, J. Russ. Phys. Chem. Soc. 1916, 48, 994).

When chlorine acts on pure benzene in sunshine, benzene hexachloride $C_6H_6Cl_6$ is formed. The substitution of chlorine for hydrogen in the nucleus or benzene ring is a very slow operation if chlorine alone is used, but if in every litre of benzene about 10 grams of iodine are dissolved, and the liquid kept boiling while a brisk current of chlorine is passed into it, substitution readily takes place and chlorinated benzenes are produced. The reaction may be continued until the whole of the hydrogen is replaced with production of hexachlorobenzene C_6Cl_6. (For the electrolytic chlorination of benzene and toluene, *see* Name and Maryott, Amer. J. Sci. 1913, (iv.) 35, 153; Fichter and Glantzstein, Ber. 1916, 49, 2473). Corresponding bromine and iodine compounds, and mono- and *p*-di-fluoro- derivatives are known.

When subjected to the action of strong nitric acid or a mixture of nitric and sulphuric acids, substitution of hydrogen by NO_2 takes place with great ease. If the mixture is kept cool only mononitrobenzene is formed, but if heated, the three dinitrobenzenes are produced, the metadinitro- product (m.p. 89°) always greatly predominating. The ortho- and para- compounds can only be produced in quantity by indirect methods. Trinitrobenzenes can only be obtained by the action of a great excess of a mixture of nitric acid and fuming sulphuric acid.

All the nitro- compounds on reduction with appropriate reagents, such as iron, zinc, or tin, in the presence of acid, preferably hydrochloric and water, yield amino- compounds corresponding with the nitro- compound reduced. Such are aniline $C_6H_5{\cdot}NH_2$, the three diaminobenzenes or phenylenediamines $C_6H_4(NH_2)_2$, &c.

The amino- compounds, by the action of nitrous acid or nitrites in the presence of an excess of acid, preferably hydrochloric, are converted into diazo- compounds. If a diazobenzene salt, *e.g.* $C_6H_5{\cdot}N_2Cl$, is dissolved in absolute alcohol, and the solution heated, the nitrogen is evolved as gas whilst benzene is regenerated. If a diazo- salt is dissolved in water and boiled in the presence of an acid, nitrogen is also evolved and the corresponding phenol is produced.

The diazo- compounds react with certain amino- compounds or phenols, giving rise to the almost innumerable series of dyes known as azo-colouring matters (*q.v.*). Solutions cooled with ice should be employed, and all rise of temperature must be carefully avoided. Under proper conditions some diazo- compounds, however, attack the *amino-* group of amino- compounds, forming diazoamino- compounds such as diazoaminobenzene $C_6H_5\cdot N : N\cdot NH\cdot C_6H_5$. These can be made to undergo an isomeric change resulting in the formation of what are known as aminoazo-compounds, of which aminoazobenzene

$$C_6H_5\cdot N : N\cdot C_6H_4\cdot NH_2$$

is a typical example. Such substances, when treated with a reducing agent, split up into an amine and a paradiamine, while diazo- compounds yield hydrazines only, and diazoamino-compounds a mixture of a hydrazine and an amine.

If the nitro- compounds are submitted to the action of alkaline reducing agents in alcoholic solution, such as a mixture of zinc-dust and alcoholic soda, the reaction takes a different course altogether. The action of alcoholic soda and heat alone will convert mononitrobenzene into azoxybenzene $C_6H_5\cdot\underset{\underset{O}{\|}}{N} : N\cdot C_6H_5$; this, by nascent hydrogen, is converted into azobenzene $C_6H_5\cdot N : N\cdot C_6H_5$, which under the action of the same reagent is still further reduced to hydrazobenzene $C_6H_5\cdot NH\cdot NH\cdot C_6H_5$. The latter, when treated with an acid, is converted into a salt of benzidine (paradiaminodiphenyl)

$$NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2$$

which is a strongly basic compound isomeric with hydrazobenzene.

When heated with concentrated sulphuric acid or treated in the cold with solutions of sulphur trioxide in sulphuric acid, sulphonic acids are produced by substitution of HSO_3 for hydrogen. These are either mono-, di-, or poly-sulphonic acids, according to the treatment adopted. They are all powerful acids, and form well-defined and generally well-crystallised salts with sodium, potassium, and ammonium, and equally definite, though less easily crystallised salts with calcium, barium, copper, iron, etc. These, especially the sodium or potassium salts, if fused with caustic potash or soda, or heated under great pressure (40 atmospheres) with aqueous soda or potash, are decomposed with production of a sulphite of the alkali metal, and conversion of the benzene residue into the corresponding hydroxy- or phenolic compound.

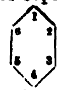
Only the methyl homologues of benzene will be considered here, as these are the chief ones which occur in coal-tar.

The monomethyl derivative is known as *toluene*, and under all treatments behaves as a completely homogeneous substance.

The dimethyl derivative is known as *xylene*, the substance of that name occurring in coal tar, which occurs as three isomeric compounds: *Orthoxylene*, boiling at 341°–142°, which, when gently oxidised with weak nitric acid, gives a toluic acid melting at 102°; *metaxylene*, boiling at 139°, which gives a toluic acid melting at 106°: *paraxylene*, melting at 15°, and boiling at 138°, giving a toluic acid melting at 178°.

Each of these different xylenes is, however, absolutely identical in percentage composition, and this isomerism is considered to be due to the *configuration* of the molecule, or, in other words, to the positions in space occupied relatively to each other, and to the benzene residue, by the two substituting molecules.

This method of regarding the constitution of benzene and its innumerable series of derivatives is usually, for purposes of discussion, investigation, or explanation, represented by drawing a hexagon to represent the molecule of



benzene, the six angles representing the six groups of CH at any of which substitution is supposed to take place. Since only one mono-substitution compound of a given kind (*i.e.* containing a given substituting group) is known, all the six CH- groups in benzene are supposed to be of equal value. The fact that disubstitution compounds exist in three distinct isomeric modifications (compare the above-mentioned xylenes), is explained in this scheme by the following suppositions as to the relative positions occupied by the substituting groups. First, substitution is supposed to take place at two adjacent angles, *e.g.* 1 and 2, 2 and 3, 4 and 5, &c., in which case the word *ortho-* is prefixed to the name of the substance, as orthodimethylbenzene (commonly called orthoxylene), or orthodichloro-, orthodibromo-, or orthodiamino-benzene, etc. Or the substitution is supposed to take place at two angles not adjacent, but with one interposing, as at 1 and 3, 2 and 4, or 1 and 5, etc. In this case the product is indicated by the prefix meta-, as metadimethylbenzene (commonly called metaxylene, &c. Lastly, the substitution is supposed to take place at opposite angles, such as 1 and 4, 2 and 5, 3 and 6, etc. In such a case the substance is known as a para- compound, as paradimethylbenzene, or paraxylene, paradinitro benzene, etc.

This theory is due to Kekulé, and satisfactorily agrees with most of the phenomena. (For a *résumé* of work on the constitution of benzene, *see* Kauffmann, Chem. Zeitschr. 4, 289; Holleman, Chem. Weekblad, 1915, 12, 440.)

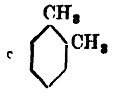
Toluene and xylene generally react under similar conditions in the same way as benzene, producing a similar series of compounds. Since, however, toluene itself is a mono- substituted benzene, mono- substituted toluenes are really di- derivatives of benzene. For instance, there is but one mononitrobenzene, but there are three mononitrotoluenes. There are three dinitro- and three diamino- benzenes, but there are six dinitrotoluenes and six diaminotoluenes, and so on.

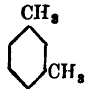
It is to be borne in mind that in all substitution derivatives higher than the di- substitution series, the number of possible modifications is greater when the substituting groups are dissimilar than when they are all alike; thus, although there are only three isomeric tri- substitution compounds of the formula $C_6H_3X'_3$ or $C_6H_3Y'_3$, there are six such compounds of the formula $C_6H_3X'_2Y'$.

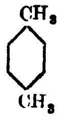
It follows that the xylenes being di- derivatives, their mono- are tri- derivatives of benzene, and consequently correspond in number with the di- derivatives of toluene.

The introduction of the methyl group, moreover, permits of another kind of substitution which gives rise to a totally different class of compounds from those described above as configurational isomerides, in which substitution takes place not in the benzene nucleus, but in the methyl group itself. Such substitution is said to be *extra-nuclear.*

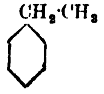
Thus, as mentioned above, there are three substances having the formula C_8H_{10} known as ortho-, meta-, or para-xylene. These isomerides are represented as dimethylbenzenes of the following configurations:—







but there is another C_8H_{10} only known to occur in one form, and always behaving as a monoderivative of benzene; this is ethylbenzene



Just as in this case a methyl group has been introduced into the methyl instead of into the nucleus, so chlorine, bromine, &c., may be introduced, and in this manner such compounds as benzyl chloride $C_6H_5 \cdot CH_2Cl$, the di- or trichloride, benzaldehyde, and many others are formed.

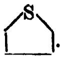
The physical properties of *toluene* greatly resemble those of benzene. As solvents, there is little or no difference in their powers, and though the boiling-point of toluene is so much higher than that of benzene, yet in a current of air at ordinary temperatures it evaporates nearly as quickly.

Toluene is a colourless limpid liquid which solidifies at −94·2° (Ladenburg and Krügel, Ber. 1899, 32, 1818) or −97° to −99° (Archibald, and McIntosh, J. Amer. Chem. Soc. 1904, 26, 305). Its specific gravity is less than that of benzene, being at 0° 0·882, at 15° 0·872, its index of refraction at 25·5° is for A 1·4709, D 1·4794, H. 1·5090 (Gladstone and Dale), at 8·5° for Hα 1·49891 (Perkin).

Toluene boils constantly at 111°, 110·56° (corr.) (Thorpe and Rodger); the vapour has much the same physiological effects as that of benzene, but its odour is decidedly less pleasant. If ingested into the stomach, it is eliminated in the urine as hippuric acid.

Of the three *xylenes* the meta- is chiefly used in commerce. Orthoxylene boils at 141°–142° 144·07° (corr.) (Thorpe and Rodger). Metaxylene boils at 139°, and its specific gravity is 0·8668 at 19°, 138·8° (corr.) (Thorpe and Rodger); sp.gr. 0·8812 (Pinette). Paraxylene boils at 138°, and at 19° its sp.gr. is 0·8621, 138·23° (corr.) (Thorpe and Rodger); sp.gr. 0·8801 (Pinette). The two former are liquid at all temperatures down to at least −20°, but paraxylene becomes solid when exposed to a freezing mixture, and when once frozen it only melts at 15°.

The xylenes are distinctly less volatile than toluene and benzene in an air current. The smell of the vapours is unpleasant and pungent, and they possess the power of producing unconsciousness when inhaled.

Both benzene and toluene when prepared from coal tar are accompanied by sulphur compounds known as *thiophens.* That derived from benzene, no doubt by the action of sulphur from the pyrites of coal at a high temperature during distillation in the gas retort, is represented by the formula C_4H_4S or .

It was isolated in 1882 by V. Meyer, who obtained by constant and repeated agitation with sulphuric acid about 2 kilos from 2000 kilos of commercial benzene. It is a colourless liquid, boiling constantly at 84°; sp.gr. at 15° 1·100. In many of its reactions it behaves exactly like benzene. *V.* THIOPHEN.

Two thiotolens corresponding with toluene, *i.e.* being methylthiophen, are known. They both boil at about 113°, sp.gr. 1·0194. The very minute quantity in which these substances occur renders them of no industrial importance, even as impurities.

Benzene was first isolated by Faraday in 1825, in the liquid separating from condensed oil gas.

It is unnecessary here to describe the processes by which Mitscherlich, D'Arcet, Kopp, and many others obtained benzene, as the first practically industrial process was that of Mansfield, founded entirely at first on Faraday's, and dealing with a similar product as the source, namely, coal tar (Mansfield, Quart. Jour. Chem. Soc. 1848, 1, 244). Mansfield took the lower boiling portion of coal tar, which was then used under the name of naphtha for lighting purposes, and distilled it over a flame in a still provided with a jacketed head and a simple form of dephlegmator made by connecting the upper part of the condensing worm with the still body by an inclined tube. The water in the jacket round the long egg-shaped head partially condensed the vapours rising from the boiling fluid until it reached a temperature of 100°, when those vapours condensable at that temperature were alone affected and returned to the still, those requiring a lower temperature passing on to the worm, and being condensed and collected. Much of the spray carried upward by the vapours was stopped in the head, and what passed it and was condensed in the connecting tube between the still head and the worm flowed into the inclined tube, and found its way back to the body of the still. Finally, when nothing more could pass the boiling water in the jacketed head, this inclined tube, on a cock being fully opened, which during the first part of the process was partially closed, could be made use of to distil over the higher boiling portions.

Such an apparatus could, of course, only effect a rough separation of the oil into a 'benzol' mainly distilling below 100° and a 'naphtha,' most of which would not distil below 100°.

If, however, the water of the water jacket round the head were carefully kept at a stated temperature, say 80°–82°, a much purer product could be obtained. For some years the process was only carried out with the object of getting oils for the Read Holliday lamp, and for the use of rubber manufacturers.

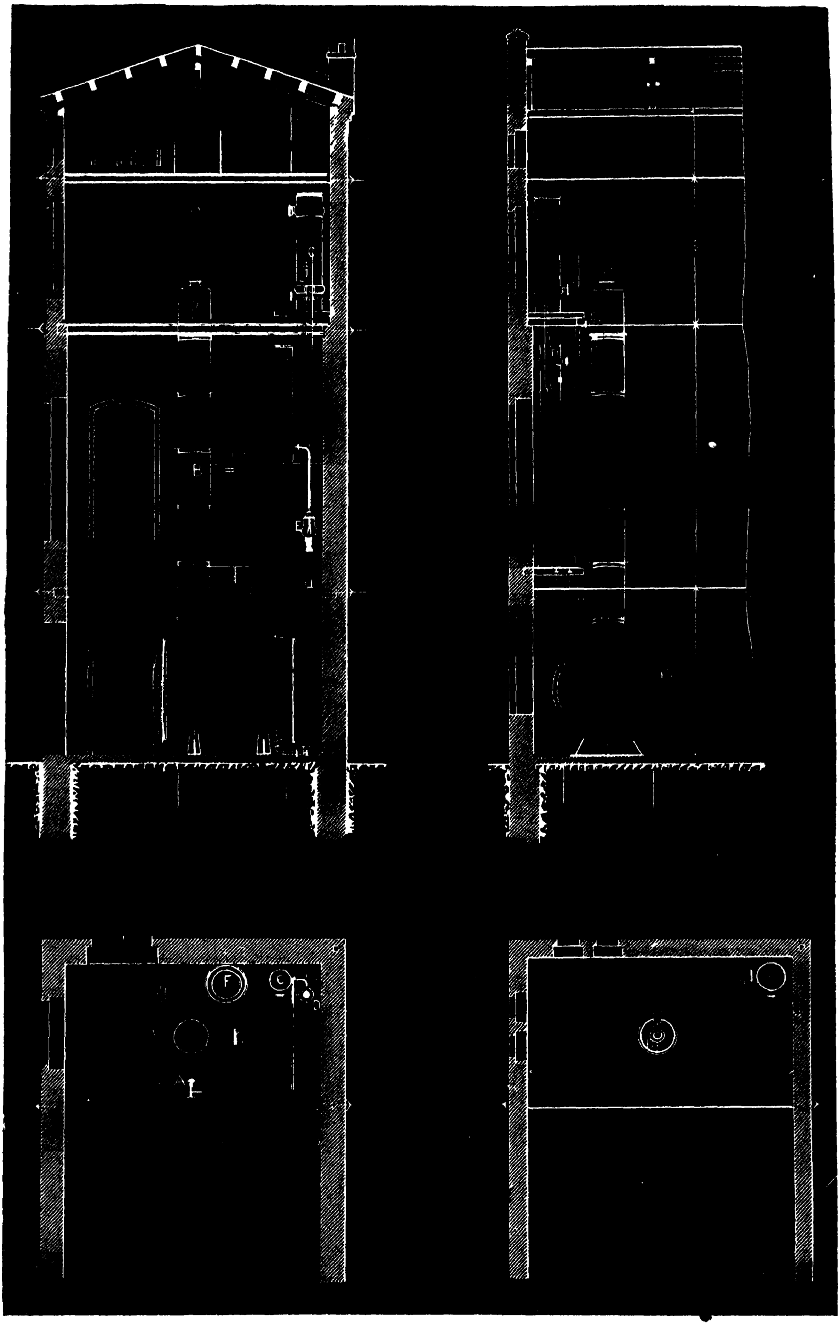


FIG. 1.

A, Still body. **B**, Analysing column. **C**, Cooler kept at temperature of distillate wanted. **D**, Condenser for pure distillate. **E**, Vase into which distillate flows. **F**, Automatic regulator.

The early demands for 'benzol' for use in the aniline colour industry were confined to what were known as 30 p.c., 50 p.c., and 90 p.c. benzols, which terms were understood to mean that 30, 50, or 90 p.c. by measure of the sample boiled below 100°. Of these the 30 p.c. was mainly used for the production of aniline for red, and the 90 p.c. for aniline for blue. Mansfield had, however, subjected his distillates to a careful but most laborious fractionation in glass retorts, finally obtaining perfectly pure benzene by recourse to freezing and pressure, and he pointed out that 'it is evident that any of the summary processes of rectification which are practised by distillers in the manufacture of alcoholic spirits are applicable to the separation of benzole from the less volatile fluids of the naphtha' (Reports of the Royal College of Chemistry, 1849, 257).

Mansfield, in fact, in the remarkable paper just quoted, laid the foundations of the whole benzene industry, and his processes with scarcely a change are in use to this day. The departures from them have been one by one abandoned in favour of his method of absolute separation of the light oils into their constituents, and it is not too much to say that had it not been for his terrible death[1] in February, 1855, we should have had the pure hydrocarbons in the market many years ago.

The introduction of the aniline black printing processes and other improvements in the dye industry, however, slowly gave rise to a demand for a purer benzene, while later on a demand for toluene and xylene stimulated the improvement of the distillation process.

The movement was naturally, as Mansfield had suggested, towards the use of such a still as had been introduced by Mr. Coffey in his patent of 1832 and subsequently carried to great efficiency by succeeding generations of spirit distillers. Coupier of Paris appears first to have worked on a large scale in this direction about 1863. He modified the original Mansfield apparatus in the way mentioned above, and showed that at one operation he could separate ordinary 50 p.c. commercial benzol as follows:—

100 *litres yielded*:

44	litres between	80°	and 82°	('Pure benzol')
6	,, ,,	82°	,, 110°	(Crude toluol)
17	,, ,,	110°	,, 112°	('Pure toluol')
5	,, ,,	112°	,, 137°	(Crude xylol)
9	,, ,,	137°	,, 140°	('Pure xylol')
13–14	,, ,,	140°	,, 150°	last runnings.

In addition there were about 6 litres between 62° and 80°, consisting of various impurities such as carbon disulphide, acetonitrile, etc.

Vedlé, Savalle of Paris, and others followed with various improvements in the same direction, Savalle being most generally considered to have produced the best still, though it had two great drawbacks, viz. it was manufactured of copper, which made it very costly, and it was hampered, as far as its condensation arrangements were concerned, by an expensive and useless attempt to use air from a fan driven by steam, as a means of cooling the condensers.

The latter attempt was soon given up. In Fig. 1 (p. 573) is seen the apparatus in its latest form as made by the Metallwerke vormals T. Aders, of Magdeburg-Neustadt.

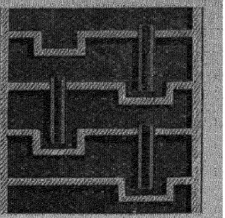


FIG. 2.

The still being charged with the proper quantity of naphtha or crude benzol, which has undergone the necessary washings with sulphuric acid and sodium hydroxide, steam is admitted into the coils, where it circulates, the condensed water escaping through another tube in the usual fashion. As soon as the liquid begins to boil, the vapour ascends into the head *a* and passes through the curved tube *a'* into the bottom of the column B. This contains 25 to 30 flat diaphragms, each pierced with a number of small holes, and one larger, into which is fitted a short wide overflow tube, the end of which stands up about 2 inches above the level of the plate. On the opposite side of the plate is a small depression about 2 inches deep and 4 inches in diameter, into which the overflow tube from the plate above dips, its own tube dipping in the same way into a depression in the plate below. The condensed fluid acts to each overflow tube as a trap (Fig. 2), and prevents the ascent of vapour through it.

The rising vapour condenses rapidly on these plates, and the fluid thus produced, unable to penetrate the small holes through which the hot vapour is rushing, rises to the brim of the overflow tube, and then pours down from plate to plate into the still body. The non-condensed vapour rises through the perforations of the next plate, where it undergoes a similar operation, and so on to the top, the vapour passing away from which has thus been successively washed by bubbling through some thirty layers of fluid, each slightly cooler than the one beneath. Finally, the vapour passes through a surface or multitubular condenser, C, which is provided with a water supply so regulated that its temperature is about that of the boiling-point of the liquid required. The liquid here condensed flows back into the column at a suitable point, while the now purified vapour passes on to the second condenser, D, and is finally completely condensed into the liquid form. Thence it flows into the glass vase E, which is fitted on to a stand-pipe communicating with the distributing-pipes which convey it to the store tanks. The fractions taken should now boil as follows: Benzene, 80°; toluene, 110°; xylene, 140°.

If pure products are required, each fraction is washed with concentrated sulphuric acid, and a washing with soda solution follows. The fraction is introduced into a cast-iron vessel provided with a lid with manhole and inlet pipe. Through the centre passes a vertical shaft rotated by mitre geared wheels. The shaft is provided with arms so arranged that the contents can be thoroughly churned up. A good form of apparatus is seen in Fig. 3. The details need no description except to point out that the screws used to force the fluids through the two vomiting tubes A and A′ should be set on the shaft with their helices reversed right and left, so that the lower one causes the lower fluid to rush up, and the upper one the upper fluid to rush down; they thus cause the two currents to meet together violently and thoroughly mingle. The centre shaft may also consist of an Archimedean screw or of a truncated hollow cone. Air agitation is not advisable on account of the loss of benzol which it is apt to cause.

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[1] Mansfield was burned to death by the boiling over of a benzene still.

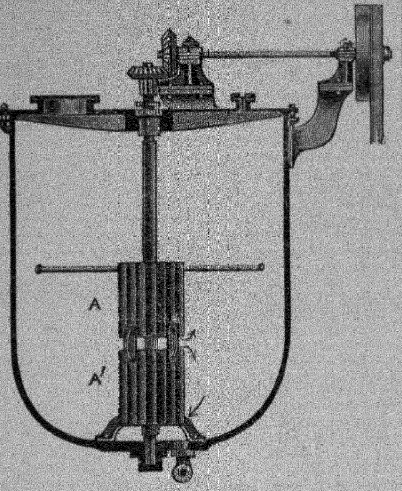

FIG. 3.

If the fraction is of fairly good quality and has been properly separated from the crude benzol or light oils, the amount of acid required need not be more than one-twentieth of its weight. In some cases, however, where the impurities are difficult to remove, more must be used, and the operation repeated. After the acid has been run off, a washing with enough soda solution to neutralise excess of acid and remove traces of phenols follows, and the fraction is then ready for a second rectification.

If crude naphtha has been used to charge the still, it will have yielded, *inter alia*, 50 p.c. or 90 p.c. benzol according to requirements. On redistillation, 100 parts of the former should yield 45–48 parts of pure benzene, and from 100 parts of the latter 70 parts of pure benzene should be obtained.

When re-rectified, the benzene and toluene should each distil constantly within 0·5° and 1·0° respectively, and the xylene within 2°.

The treatment for obtaining toluene is exactly the same as that described for benzene, the toluene following the benzene from the crude benzol still and being subsequently re-rectified. Toluene is also accompanied by the corresponding thiophen (thiotolen), and requires very careful and thorough washing with sulphuric acid, or it cannot be properly nitrated.

After the separation of the toluene, more or less crude xylene is obtained, and the residue in the still is then cooled and run out. When good crude benzol has been worked, the residue contains a very large quantity of naphthalene, which separates from it when cold, and is known in the works as 'naphthalene salts.' As it has all been brought off from the tar at a low temperature, it is extremely free from higher boiling substances, and very pure naphthalene can be obtained from it with little trouble. Of the rest, some 20–30 p.c. consists of phenol, to which the same remarks apply. The remaining third consists of a mixture of hydrocarbons from which some more xylene could no doubt be recovered, but the bulk of this 'dead oil,' as it is often called, is used for burning. Metaxylene can be prepared from the purified mixed xylenes by agitation with sulphuric acid, as described for benzene and toluene, to remove the thiophens, when a subsequent treatment with its own weight of sulphuric acid converts the metaxylene into a sulphonic acid, which after separation from the insoluble portion is hydrolysed, and metaxylene of great purity obtained.

Benzene, it is stated, is formed by passing the vapour of petroleum mixed with hydrogen through a tube containing a suitable catalyst,—iron, copper, zinc, nickel, &c.—at a temperature between 180° and 300° (Eng. Pat. 17272, 1913; 20470, 1913; 2838, 1914).

Benzene and toluene may be obtained by the demethylation or 'cracking' of the higher benzenoid hydrocarbons. The optimum temperatures for the production of benzene and toluene are respectively 800° and 750°, the solvent naphtha containing the higher hydrocarbons being passed through a heated steel tube under a pressure of 11 atmospheres. About 25 p.c. of the solvent naphtha is demethylated, the percentage yields of benzene and toluene at the foregoing temperatures being 15·9 and 20·6 respectively (Egloff and Moore, J. Soc. Chem. Ind. 1917, 36, 128; G. T. Morgan, Report for 1917, J. Soc. Chem. Ind.).

Valuation of Commercial 'Pure Benzol.'—As stated above, the whole should boil within 0·5° of the correct boiling-point. It should give no crystalline precipitate on standing with a few drops of phenylhydrazine (test for carbon disulphide). When shaken with concentrated sulphuric acid the latter should be only slightly darkened (thiophen or aliphatic hydrocarbons). On shaking with sulphuric acid and a trace of isatin, no blue colouration should be produced (thiophen). On treatment with a mixture of nitric and sulphuric acids, and subsequent distillation in a current of steam, no unnitrated hydrocarbons should be obtained (aliphatic hydrocarbons). Lastly, it should solidify when cooled below 0°.

Pure toluene of commerce should not impart any colouration to sulphuric acid when shaken with it. On shaking 90 c.c. of toluene with 10 c.c. of nitric acid (sp.gr. 1·44) in a stoppered bottle, the acid should assume only a red colour, and remain quite clear and bright, not turning greenish or blackish. (For much information as to the commercial valuation of 'benzols,' *see* Lunge, Coal Tar and Ammonia, 5th ed. 1916; and Northall-Laurie, Analyst, 1915, 40, 384; James, J. Soc. Chem. Ind. 1916, 35, 236; Spielmann and Jones, *ibid.* 911; 1917, 36, 489; Spielmann and Wheeler, *ibid.* 396; Edwards, *ibid.* 587; Wilson and Roberts, J. Gas Lighting, 1916, 134, 225; Harker, J. Roy. Soc. New South Wales, 1916, 50, 99; Egloff, Met. and

Chem. Eng. 1917, 16, 259; Jones, J. Soc. Chem. Ind. 1918, 37, 324; Weiss, J. Ind. Eng. Chem. 1918, 10, 1006.)

Nitration of Benzene, Toluene, etc.—Nitrobenzene first made its appearance in the arts under the name of *essence de myrbane*, manufactured in France by Collas. It was used to scent soap and as a bitter-almond flavouring. Mansfield had taken out a patent for its manufacture in 1847 from coal-tar benzene. The usual arrangement now adopted for its manufacture (*see* Fig. 4) is as follows:[1]—

The nitrating pan has a total capacity of 1600 gallons, and is capable of treating 500 gallons or 4420 lbs. of benzol in one charge. It is of cast iron, 1½ inches thick, the sides, from the lid down to a depth of 3 feet, being ¼ inch thicker. The vertical agitating shaft is suspended from the lid on ball bearings, and carries two propellor agitators. The internal cooling pipes consist of two separate coils of thin lead pipe 2 inches diameter, each coil being about 150 feet long. They are supported on circular cast-iron grates or tables, as shown. The coils are spaced out so as to allow free passage of the liquid between them. To direct the upward flow of the liquid, the lower propellor agitator is surrounded by a cast-iron cylinder with large perforations at the bottom to admit the descending liquid. This serves also as a support for the grates and coils. Five hundred gallons of pure benzol are first run by gravity into the machine. The acid-mixing tank, which stands

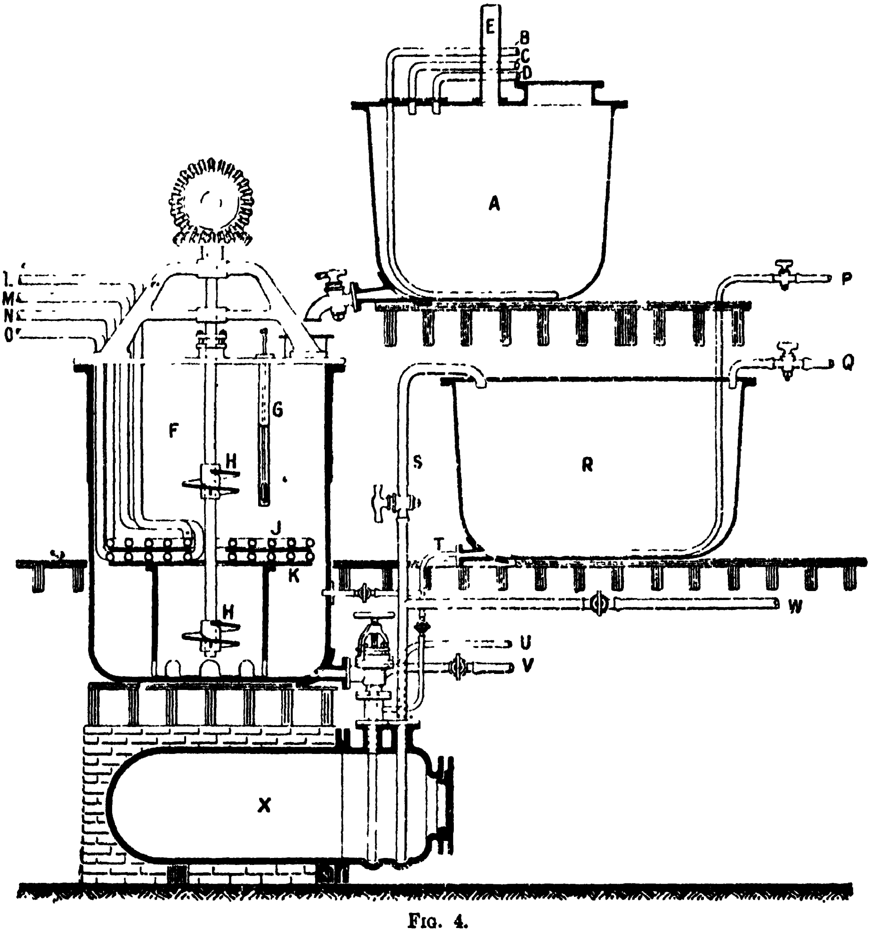

Fig. 4.

A, Mixed-acid pan.
B, Compressed-air pipe.
C, Sulphuric acid inlet.
D, Nitric acid inlet.
E, Acid-vapour pipe.
F, Nitrobenzene pan.
G, Thermometer.
H, Propeller agitator.
J, Lead cooling-coils.
K, Supporting grids.
L, Cooling-water outlet.
M, do. do. do.
N, Cooling-water inlet.
O, Do. do. do.
P, Compressed-air pipe.
Q, Water inlet.
R, Nitrobenzene washpan.
S, Pipe from egg.
T, Nitrobenzene pipe.
U, Compressed-air pipe.
V, Waste-acid pipe.
W, Pipe to N. B. tank.
X, Air-pressure egg.

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[1] See Chem. Trade Jour. 1906, 38, 59. The writer is indebted to Messrs. Davis Bros. for permission to reproduce the sketch of the apparatus.

bove, is charged with 5000 lbs. of nitric acid, ·43 sp.gr. or 86°Tw., and 6600 lbs. of sulphuric cid of 96 p.c., and these are thoroughly mixed by ir agitation. In some factories the acids are ixed in the above proportions in large stock nks. The mixed acid is run in a thin stream to the benzol, while the agitators are revolving t a speed of about 60 revs. per minute. The eat of the reaction is indicated on a long ermometer suspended in a metal tube, which asses through the lid and dips into the liquid. he temperature is kept below 60° by checking e flow of acids if the temperature rises. With good supply of cooling water passing through he coils, very little attention is required, and he process, which a few years ago was attended ith danger and frequent loss, is now carried n almost automatically. This is principally wing to the purity of the benzol employed, and he use of internal cooling coils in place of the utside water-jacket.

It is important that the coils should be of ure chemical lead, without flaw, and before eing used, they should be examined minutely. ome of these coils have been known to work early 4 years continuously. The vertical ortions, connecting the coils with the exterior, ould be protected, as these are quickly ttacked. This is done by 'threading' them rough lead pipes of slightly larger diameter, nd filling up the intervening space with any cid-proof cement. After the full charge of ixed acids has been run into the machine, e agitation is continued for about 4½ hours, nd the benzol will then be completely transformed into nitrobenzol. If a sample is then ken while the agitators are running, and llowed to settle, the weak sulphuric (called aste acid) will contain less than 1 p.c. of nitric cid, and the upper layer of nitrobenzol will ave a sp.gr. of 1·235. The agitation is then opped, and the contents of the machine llowed to settle for 5 hours. The 'waste cid,' having settled to the bottom, is run off to the air-pressure egg below, and blown to e sulphuric acid concentrating department to e rectified. The nitrobenzol is next run off to the air-pressure egg and blown into the ashing pan above, where it is washed by iolent air agitation with an equal volume of ater containing sufficient sodium hydroxide neutralise any trace of acid left in it. After ettling a few hours the nitrobenzol settles to e bottom, and is run down into the air-pressure gg, and forced from there into a large store tank, hich is set at a high level, so that the contents an run by gravity to the aniline machine. he wash-water, which contains a little nitroenzol in suspension, is run into a series of ettling tanks, and the oil recovered. Although is possible to work a charge of benzol in each achine daily, it is customary to have a duplicate et of machines, and to work each machine on lternate days. For an output of 150 tons of ure aniline oil per month, six nitrobenzol achines are required, with their corresponding djuncts, as shown in the figure. The yield of itrobenzol from the pure benzol employed is 54½ p.c. by weight, and this approaches so ear the theoretical yield, viz. 157·6 p.c., that ere is little room for improvement. It is ossible slightly to increase this yield by settling the waste acid for 48 hours in a series of tanks, and skimming off the nitrobenzol, but in practice it has not been found to pay for the trouble, especially if the previous separation be carefully watched.[1] Several plants have been proposed for the continuous process of nitration of benzene, the hydrocarbon and nitrating acid being led into the apparatus at certain points and the nitrobenzene emerging at another (*see* Cain, The Manufacture of Intermediate Products for Dyes, Macmillan, 1918).

For a cryoscopic method of determining nitrobenzene in commercial nitrobenzenes, *see* Simpson and Jones, J. Soc. Chem. Ind. 1919, 38, 325; Analyst, 1919, 379.

When the nitrobenzol is to be sold as 'myrbane,' it is distilled under diminished pressure in order to obtain a perfectly clear and transparent liquid such as the users of myrbane demand. It is customary to use toluene imperfectly freed from benzene for this purpose, that article being cheaper and yielding a somewhat more fragrant myrbane than benzene alone.

The treatment adopted with toluene and xylene is in all essential particulars the same as with benzene. In the former case, however, if the nitrotoluene is not employed direct, the product is separated into *p*- and *o*-nitrotoluene by fractional distillation under diminished pressure through a Savalle column. The distillation is stopped when 40 p.c. has distilled, and the distillate on redistillation gives nearly pure *o*-nitrotoluene (b.p. 233°). The residue on cooling deposits crystals of *p*-nitrotoluene (b.p. 238°; m.p. 54°), which are freed from oil by centrifugating.

(For the estimation of *o*- and *p*-nitrotoluene, *see* Reverdin and De la Harpe, Bull. Soc. chim. 1888, (ii.) 50, 44; Glasmann, Ber. 1903, 36, 4260; Chem. Zeit. 1904, 28, 187; Holleman, Proc. K. Akad. Amsterdam, 1904, 7, 395; Rec. trav. chim. 1908, 27, 458.)

Dinitrobenzene and *dinitrotoluene* are obtained by treating a charge of the hydrocarbon with double the proportion of the mixed acids, the operation being carried out in two stages, and the second charge of acids run in directly after the first. The cooling water is shut off and the temperature allowed to rise rapidly. Or nitrobenzol already manufactured may be taken and again treated with the necessary acid.

The product of the reaction is separated from the acid as usual, and then thoroughly washed with cold, and lastly with hot, water. As dinitrobenzene is sensibly soluble in the latter, the hot wash-water had better always be preserved and used for first washing a subsequent batch. Finally, it is allowed to settle, and, while still warm, run out into iron trays, in which it solidifies in masses 2 to 4 inches thick. The principal product of the reaction is meta-dinitrobenzene, m.p. 89·8°, but **orthodinitrobenzene**, m.p. 118°, and **paradinitrobenzene**, m.p. 172°, are also produced, the m.p. of the commercial product being about 85°–87°. It should not contain any nitrobenzene, and should be well crystallised, hard, and almost odourless, and should not render paper greasy.

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[1] Benzene may also be nitrated by using sodium nitrate instead of nitric acid. For example: 85 kilos. of benzene and 115 kilos. of sodium nitrate are mixed at 60°–80°, and 150 kilos. of 90–96 p.c. sulphuric acid added slowly. The temperature rises to about 100°, when 65 kilos. of benzene are added, and when the nitration is complete the lower layer of bisulphate is drawn off. The yield is stated to be 150–154 kilos. of washed nitrobenzene, sp.gr. 1[illegible]8 at 15°, or 148 kilos. of the pure substance boiling at 96° under a pressure of 18 mm. (Saccharin-fabrik. Akt.-Ges. vorm. Fahlberg, List & Co. D. R. P. 221787; F. P. 401679).

Dinitrotoluene is prepared by a process similar to the above, and, since ortho- and para-nitrotoluene yield, when nitrated at a high temperature, most of the 2 : 4-dinitrotoluene, it is better to proceed straight on from the toluene.[1]

The subsequent treatment is the same as when dinitrobenzene is manufactured. Commercial dinitrotoluene consists mainly of the last-named and the 2 : 6- modifications, but always contains small quantities of the other isomerides. The 2 : 6- only occurs in small proportion, and mainly in the oily drainings from the crude product. The nitration of the pure metaxylene does not differ from the processes already described.

To obtain the more highly nitrated derivatives nitrosyl sulphate may be employed. *m-Dinitrobenzene* (1 part) is slowly heated with nitrosyl sulphate (2 parts) until dissolved, when nitric acid (2 parts) is added and the mixture maintained at 100°–120° until *s-trinitrobenzene* is produced (Heinemann, Eng. Pat. 102216 of 1915).

Trinitrotoluene. There are six possible isomerides of this compound, viz. :—

		m.p.
α or 2.4.6	trinitrotoluene . .	80·8°
β or 2.3.4	„ . .	112°
γ or 2.4.5	„ . .	104°
δ or 3.4.5	„ . .	137·5°
ε or 2.3.5	„ . .	97·2°
ζ or 2.3.6	„ . .	79·5°

All of them are of practically equal value as explosives, but the best-known is the α-compound, the product known as T.N.T., or trotyl or trilite. The other isomerides in the commercial product are derived from *m*-nitrotoluene, which is present in the ordinary mononitrotoluene to the extent of 4–5 p.c. The various trinitrotoluenes give different colourations with acetone and ammonia, viz. α, deep red; β, greenish-yellow; γ, blue; ζ, orange-red; and ε, rose-red.

In the manufacture of α-trinitrotoluene (T.N.T.), mononitrotoluene is first prepared by using the waste acid resulting from the manufacturing process. The nitration is carried out in a jacketed apparatus provided with rotating arms. The toluene is run into the apparatus, and whilst it is kept agitated, the waste acid and fresh nitric acid are added. The temperature is kept below 30°. After setting for six hours the mononitrotoluene is separated from the waste acid. To the latter fuming sulphuric acid and nitric acid are added. This fresh mixture is added to the mononitrotoluene in the agitating vessel, and kept in continuous motion for six hours at a temperature of 90°. The steam is then shut off in the jacket, agitation is discontinued, and cold water and finally a refrigerated liquid at 2° are passed round the jacket. The dinitrotoluene is thus crystallised out in the mixing vessel, and the waste acid can be run off. The latter is revivified by the addition of fuming sulphuric acid, and this fresh mixture is added to the dinitrotoluene. After warming and agitating nitric acid is added and the temperature raised very gradually to 92°. After heating for twenty hours the whole of the contents of the vessel is run into cooling tanks, where the trinitrotoluene is allowed to crystallise out slowly, during some four to five days. The waste acid is then separated and used for the preparation of mononitroluene. The trinitrotoluene is washed with water, ground under edge runners, and finally washed in an alkali solution. It is then dissolved in acetone, and sodium carbonate is added. The solution is heated in a steam-jacketed vessel for four hours, after which the acetone is distilled off and condensed, and the molten trinitrotoluene is run into cooling vessels to crystallise out. The crystals are thoroughly washed with water, dissolved in hot 96 p.c. alcohol, the solution filtered and allowed to crystallise (Vasquez, Z. ges. Schiess- u. Sprengstoffw. 1911, 6, 301; J. Soc. Chem. Ind. 1911, 30, 1046).

Langenscheidt (Z. ges. Schiess- u. Sprengstoffw. 1912, 7, 425) describes the process as follows:

A mixed acid (1400 kilos), consisting of equal quantities of sulphuric acid and nitric acid (94–95 p.c.), is allowed to flow slowly into a cast-iron vessel containing a solution of orthonitrotoluene (500 kilos) in sulphuric acid (1400 kilos of 100 p.c. acid) which has been warmed to 60°–70°. This vessel is steam-jacketed, and has also water-cooling coils, and a screw agitator, which runs at about 182 revolutions per minute. At the commencement the temperature of the mixture is prevented from rising by means of the water coils until the whole of the orthonitrotoluene is converted into dinitrotoluene. Steam is now passed through the jacket to start the conversion of the dinitrotoluene into trinitrotoluene, and the temperature is not allowed to rise above 150°. When nitration is complete, the temperature is maintained at this point for one hour. It is then allowed to fall to 100°, and 200 litres of water are added in order to increase the yield. The molten trinitrotoluene is separated from the acid and washed until neutral. This product has a m.p. of 72°–74°, and is used in the ammonium nitrate class of explosives. To produce the trinitrotoluene of higher m.p. (81°–82°), which is used for filling shells, the lower melting product (500 kilos) is dissolved in 2300 litres of a mixture of 90 p.c. alcohol containing 5–10 p.c. of benzene, and, after filtering, the solution is crystallised in a water-jacketed enamelled pan. By evaporating the mother liquor to one-third of its bulk, a quantity of brownish-coloured crystals are obtained, which are used in the ammonium nitrate class of explosives, whilst, on further evaporation, a dark-brown or red liquid (16·6–17·2 p.c. N) is obtained, which is used in the explosive industry for gelatinising collodion cotton under the name of liquid trinitrotoluene (J. Soc. Chem. Ind. 1912, 31, 1147).

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[1] For a detailed description of the manufacture, see Kayser, Zeitsch. Farb. Ind. 1903, 2, 16, 31. *Cf.* Kidokoro, J. Chem. Ind. Tokyo, 1917, 20, 460; J. Soc. Chem. Ind. 1917, 36 1065.

The chief difficulties in the nitration process are due to the presence of inorganic impurities, chiefly lead and iron salts, derived from the sulphuric acid and from the action of the nitrating acid on the apparatus, and organic by-products formed by sulphonation, oxidation, and reduction. Among the by-products may be: (1) Trinitrobenzoic acid or tetranitromethane, owing to oxidation in case of overheating or pressure; the last-named may be recognised by its intense odour; metallic salts may act as catalysts in promoting oxidation. (2) Phenolic compounds, such as cresols, formed by the reduction of the nitro- compounds by hydrogen produced by the action of the nitrating acid on the apparatus, the amino- compounds being then converted into diazo- and hydroxy-compounds; in presence of metallic salts, highly explosive salts of nitro-cresols may be formed. (3) Sulphonic acids owing to too low a concentration of nitric acid. To obtain good results the following conditions should be observed: (1) The amount of nitric acid used should exceed the theoretical quantity by at least ½ mol. (2) The degree of nitration should be controlled by the concentration of nitrating acid, temperature, and duration of reaction rather than by the actual quantity of nitric acid used. (3) The reaction product should be separated from the spent acid as quickly as possible. (4) The action of the nitrating acid on the apparatus should be reduced to a minimum by suitable choice of material and concentration of acid (Copisarow).

The following bibliography has been compiled by Copisarow (J. Soc. Chem. Ind. 1915, 34, 1169):—

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For mode of inspection and testing of commercial trinitrotoluene, *see* Stevens, J. Ind. Eng Chem. 1917, 9, 801; J. Soc. Chem. Ind. 1917, 36, 1029. J. C. C.

BENZENEAZOSALICYLIC ACID is obtained by diazotising a cooled mixture of aniline and hydrochloric acid with sodium nitrite, and adding the diazonium chloride to an aqueous solution of sodium salicylate when the yellow sodium salt of the azo- compound is formed (Fischer and Schaar-Rosenberg, Ber. 1899, 32, 81).

BENZENE DIAZONIUM SALTS *v.* DIAZO COMPOUNDS.

BENZENE SULPHONIC ACIDS.

Benzene sulphonic acid (*phenyl sulphurous acid, sulphobenzolic acid*) $C_6H_5{\cdot}SO_3H$ may be prepared by shaking benzene with fuming sulphuric acid, or by passing benzene vapour into heated sulphuric acid; by oxidising benzene sulphinic acid; by boiling *p*-diazobenzene sulphonic acid with alcohol.

On the large scale it is made as an intermediate product for the manufacture of phenol by sulphonating benzene in a closed cast-iron steam-jacketed pan fitted with a helical stirrer. For details of the various methods of carrying out this operation, *see* Cain's Intermediate Products for Dyes, Macmillan and Co., 1918. The free acid is best obtained by decomposing the lead or barium salt with sulphuric acid. Forms small deliquescent plates containing 1½ mols. H_2O.

Benzene-m-disulphonic acid $C_6H_4(SO_3H)_2$. Obtained by the further action of sulphuric acid upon benzene, or on the preceding compound, at a temperature of 240°–250°. At higher temperatures, or under the influence of catalysts (mercury, ferrous sulphate), the *p*-isomeride is formed in addition. Lamberts (D. R. P. 113784) employs as sulphonating agent *sodium hydrogen disulphate* $NaH_3(SO_4)_2$ (obtained by heating acid sodium sulphate with sulphuric acid). This is mixed with benzene and heated to 200°, treated with milk of lime, and the solution of the sodium benzene-*m*-disulphonate filtered off and evaporated. The free acid forms very deliquescent crystals containing 2½ mols. H_2O.

Benzene-tri-sulphonic acid $C_6H_3(SO_3H)_3$, prepared by heating an alkaline salt of the mono- or *m*-disulphonic acid with sulphuric acid until the sulphuric acid volatilises.

BENZIDINE and **BENZIDINE REARRANGEMENT** *v.* DIPHENYL.

BENZIDINE AZO- DYES *v.* AZO- COLOURING MATTERS, and DISAZO- and TETRAZO- COLOURING MATTERS.

BENZIDINEDISULPHONIC ACID *v.* DIPHENYL.

BENZIDINE PUCE *v.* AZO- COLOURING MATTERS.

BENZIL *v.* KETONES.

BENZINE, Light petroleum (*v.* PETROLEUM).

BENZINOFORM. Syn. for carbon tetra chloride (*q.v.*).

BENZO-AURINE, -BLACK BLUE, -BLUE, -BROWNS, -FAST PINK, -FAST SCARLETS, -INDIGO BLUE, -GREY, -OLIVE, -ORANGE,

-PURPURINS, -RED BLUE, -VIOLET *v.* AZO-COLOURING MATTERS.

BENZOFLAVINE *v.* ACRIDINE DYESTUFFS.

BENZOIC ACID $C_7H_6O_2$ or $C_6H_5{\cdot}CO_2H$. (*Acide benzoïque*, Fr.; *Benzoësäure*, Ger.) *Acidum benzoicum.* Blaise de Vigenère, in his Traité du feu et du sel, published in 1608, described the preparation of benzoic acid by sublimation from gum benzoïn. Lemery, in 1675, called attention to its acid properties; and Scheele showed, in 1775, that it could be extracted from gum benzoïn by boiling the gum with lime, concentrating the solution, and decomposing the salt with hydrochloric acid. Scheele also, in 1785, obtained benzoic acid from cow's urine; but it was not until 1829 that Liebig showed that the substance contained in the urine, by the decomposition of which benzoic acid is formed, is hippuric acid.

Occurrence.—Benzoic acid occurs in gum benzoïn, tolu balsam, storax, dragon's blood, and various other natural resins; in oil of bergamot and oil of cinnamon; in vanilla, calamus root, and the ripe fruit of the clove tree; in various sweet-smelling flowers—thus in the flowers of *Unona odoratissima*, from which the perfume *ylang-ylang* is prepared; as hippuric acid (and sometimes even, it is asserted, as free benzoic acid) in the urine of herbivora; and in *castoreum*, a viscid, fœtid secretion, found in pouches situated in the perinæum of the beaver.

Formation.—By the oxidation of all compounds which contain the phenyl group united to a single lateral chain, such as toluene, benzyl chloride, benzyl alcohol, benzaldehyde, cinnamic acid, &c. By heating benzotrichloride $C_6H_5{\cdot}CCl_3$ with water. By heating benzonitrile $C_6H_5{\cdot}CN$ with acids or alkalis. By boiling hippuric acid with hydrochloric acid

$$(C_7H_5O)NH{\cdot}CH_2{\cdot}CO_2H+H_2O$$
$$=C_7H_6O_2+NH_2{\cdot}CH_2{\cdot}CO_2H.$$

By passing carbon dioxide into benzene containing aluminium chloride

$$C_6H_6+CO_2=C_6H_5{\cdot}CO_2H.$$

Preparation.—1. *From gum benzoïn.* In order to obtain the acid from gum benzoïn by sublimation, the gum, broken up into small pieces, is introduced into a flat iron vessel, over the mouth of which filter paper is then pasted. A large conical cap of strong paper, exactly fitting the iron vessel, is placed over the filter paper, tied round the rim, and the whole is gently heated over a sand-bath at a temperature of about 170°. The benzoic acid sublimes through the filter paper and collects in colourless crystals inside the paper cone, from which it is removed at the end of the operation (Mohr, Annalen, 29, 177). The yield is about 4 p.c. of the gum employed, and from three to four hours are required for the sublimation of a pound of benzoic acid. A trace of an aromatic oil from the gum adheres to the crystals, imparting to them a pleasant odour of vanilla, and enhancing their value as a pharmaceutical preparation. On a manufacturing scale a modification of the foregoing laboratory process is employed, in which the gum is heated in a closed vessel and the vapour of the subliming acid flows over into a side chamber and condenses at a point below the source of heat, thus obviating all risk of fusing the sublimate. The gum benzoïn is introduced by means of a metal drawer, which is heated from beneath by gas-jets; whilst the sublimed acid collects in a second drawer, and can thus be removed at the end of the operation (comp. Starting, Arch. Pharm. 231, 342). By other methods the yield from gum benzoïn may be increased to 25 p.c.

Wöhler's method (Annalen, 49, 245) consists in dissolving the powdered gum in an equal volume of alcohol of 90–95 p.c., adding fuming hydrochloric acid to the hot solution until a precipitate begins to be formed, and distilling the mixture. The distillate contains ethyl benzoate, alcohol, and hydrochloric acid. The residue is again distilled with water as long as ethyl benzoate passes over, and the united distillates are boiled with caustic potash to decompose the ethyl benzoate. From the solution the benzoic acid is precipitated with hydrochloric acid. It smells like the sublimed product.

Scheele's method of extracting the benzoic acid from the gum with slaked lime and water (*v. supra*), may also be employed.

2. *From urine.* The urine of the cow or horse is allowed to putrefy, so as to induce a hydrolytic decomposition of the hippuric acid into benzoic acid and glycocoll. Milk of lime is then added, the filtered solution is evaporated to a small bulk, and the benzoic acid precipitated with hydrochloric acid. In order to avoid the evaporation and the attendant disagreeable smell, the excess of lime may be removed by carbon dioxide, the benzoic acid precipitated by the addition of ferric chloride, and the ferric benzoate, after separating it by filtration, decomposed by hydrochloric acid. The acid thus prepared smells of urine, and must not be used in medicine. The smell may, however, be removed or concealed by mixing the acid with a small quantity of gum benzoïn and subliming it.

The fresh urine may also be evaporated to one-third of its bulk, filtered, mixed with hydrochloric acid, and allowed to cool. Hippuric acid crystallises out, which, by boiling with concentrated hydrochloric acid, is decomposed into glycocoll hydrochloride and benzoic acid. Benzoic acid may also be prepared by the action of ammonia and zinc-dust on gallic acid and catechu-tannic acid (Guignet, Compt. rend. 113, 200).

3. *From toluene.* Most of the benzoic acid employed at the present day, and certainly all that is employed in the coal-tar colour industry, is manufactured from toluene (*v. infra*). Toluene by oxidation with nitric acid, may be directly converted into benzoic acid; but it is better to chlorinate it first to benzyl chloride, which is more readily attacked by the oxidising agent. Lunge and Petri (Ber. 10, 1275) boil benzyl chloride (1 part) and dilute nitric acid (3 parts of acid of 35° Baumé with 2 parts of water) in a reflux apparatus until the smell of benzyl chloride and benzaldehyde is no longer perceptible. A. v. Rad (Dingl. poly. J. 231, 538), however, states that this method is unsuited for preparing the acid on a manufacturing scale, and prefers to decompose benzotrichloride by heating it with water under pressure:

$$C_6H_5{\cdot}CCl_3+2H_2O=C_6H_5{\cdot}CO_2H+3HCl;$$

but it is difficult to prepare pure benzotrichloride, and the benzoic acid manufactured by this process is always contaminated with chlorobenzoic acids formed from chlorinated benzotrichlorides.

Espenschied (D. R. P. 47187) boils the benzotrichloride with milk of lime, or with a solution of caustic soda mixed with whiting or other insoluble matter, the presence of which aids the reaction by preventing the benzotrichloride from forming a separate layer and also by promoting local superheating.

E. Jacobsen (D. R. P. 11494 and 13127) heats benzotrichloride with acetic acid to which a little zinc chloride has been added:

$$C_6H_5{\cdot}CCl_3+2CH_3{\cdot}CO_2H=C_6H_5{\cdot}CO_2H+2CH_3{\cdot}COCl+HCl$$

The acetyl chloride is distilled off, the residue extracted with sodium carbonate, and the benzoic acid precipitated with hydrochloric acid.

P. Schulze (D. R. PP. 82927, 85493) heats benzotrichloride with lime-water in the presence of some iron powder. In order to avoid the formation of chloro-derivatives, the direct oxidation of toluene either by nitric acid or by manganese dioxide and sulphuric acid, has been suggested (*see* D. R. PP. 101222, 107722, 175295, 216091).

The Weston Chem. Co. and J. Savage (Eng. Pat. 116348) convert benzyl chloride into benzyl alcohol by boiling with sodium hydroxide solution or milk of lime, and oxidising the alcohol to alkali benzoate by hypochlorite in presence of alkali.

The benzoic acid required in the coal-tar colour industry is obtained as a by-product in the manufacture of benzaldehyde by heating benzal chloride with milk of lime (*v.* BENZALDEHYDE), a portion of the benzaldehyde being converted into calcium benzoate in this process.

4. *From coal-tar oil.* Aktiengesellschaft fur Theer und Erdöl Industrie, Eng. Pat. 7867; D. R. P. 109122; J. Soc. Chem. Ind. 1899, 785. The carbolic or creosote oil fraction, obtained from coal tar, and boiling between 160° and 240°, contains benzonitrile. The fraction from which phenol is obtained is washed with dilute soda lye (sp.gr. 1·1) to remove the phenol and cresol, and the remaining oil placed in a jacketed vessel, provided with an agitator and connected with a condenser and receiver. Caustic soda lye (sp.gr. 1·4) is added in about twice the quantity corresponding to the benzonitrile present. The mixture is agitated, and wet steam passed in for some hours, as long as ammonia is evolved in considerable quantity. The receiver then contains the lower boiling constituents of the oil, together with a somewhat concentrated ammonia solution, whilst the contents of the still consist of a lower alkaline layer and an upper oily one. The former is neutralised with carbonic acid or a mineral acid, separated from traces of phenol or resinous matters, and the resulting solution of sodium benzoate decomposed whilst hot by adding an excess of acid. On cooling, pure benzoic acid separates in white crystals.

5. *From the naphthols and other naphthalene derivatives.* Basle Chemical Works, J. Soc. Chem. Ind. 1901, 1139; D. R. P. 136410; Fr. Pat. 313187; Eng. Pat. 15527; U.S. Pat. 702171. (*See also* Chem. Zentr. 1903, i. 546, 857, 1106; D. R. PP. 138790, 139956, 140999.) By heating the naphthols or other naphthalene derivatives to about 250°, in presence of alkali with metallic oxides or peroxides such as copper or iron oxide, barium, lead or manganese peroxide, they yield phthalic and benzoic acids, and a few intermediate products. The excess of alkali is removed by lixiviation with a little water; the acids are then dissolved in water and decanted from the reduced oxide. This solution is saturated with carbon dioxide and filtered from unchanged naphthol. The filtrate is decomposed with sulphuric acid and evaporated, the precipitated acids being purified by distillation.

6. *By the electrolytic oxidation of phenanthrene.* Farbwerke vorm. Meister, Lucius and Brüning, Chem. Zentr. 1904, ii. 71; D. R. P. 152063.

Properties.—It crystallises in lustrous leaflets or flat needles of sp.gr. 1·2659 15°/4°, melting at 121·4°. It boils at 249°, but is volatile even at 100°, so that it may readily be sublimed; the vapour excites coughing. It may be distilled with steam; 2 litres of aqueous distillate contain 1 gram of benzoic acid. 100 parts of water dissolve at

4·5°	10°	81°	75°
1·823	2·068	4·247	21·931

(Ullmann, Enzyklop. ii.); it is soluble in about twice its weight of ether and in about its own weight of absolute alcohol at ordinary temperatures.

Traces of impurity lower the melting-point of benzoic acid very considerably. The impure acid is also deposited from its solutions in smaller crystals than the pure.

(For *absorption spectra, see* Hartley and Headley, Chem. Soc. Trans. 1907, 319.)

Reactions.—When heated with *lime*, benzoic acid yields benzene and calcium carbonate (Mitscherlich). It is very stable towards oxidising agents; dilute *chromic acid* is without action on it, but by warming it with *manganese dioxide and sulphuric acid* it is converted into formic acid, carbon dioxide, and phthalic acid—the latter being formed by the simultaneous oxidation of formic and benzoic acids (Carius, Annalen, 148, 72). *Sodium amalgam* reduces benzoic acid in boiling alcoholic solution to benzyl alcohol, benzaldehyde, and tetrahydrobenzoic acid (Aschan, Ber. 24, 1864, and Annalen, 271, 231). By electrolytic reduction, benzaldehyde is obtained (Mettler, Ber. 41, 4148), and by reduction with hydrogen and platinum, hexahydrobenzoic acid is the chief product (Willstätter and Mayer, Ber. 41, 1479). When distilled over heated *zinc-dust* it yields benzaldehyde (Baeyer, Annalen, 140, 296). Calcium benzoate yields on distillation benzophenone $C_6H_5{\cdot}CO{\cdot}C_6H_5$, together with a small quantity of benzene and anthraquinone $C_{14}H_8O_2$ (Kekulé and Franchimont, Ber. 5, 908). Taken internally, benzoic acid is excreted in the urine as hippuric acid (Wöhler).

When a solution of ferric chloride which has been mixed with sufficient ammonia to turn it dark-red is added to a solution of a benzoate, a flesh-coloured precipitate of basic ferric benzoate $(C_7H_5O_2)_3Fe,Fe(OH)_3$ is formed. This reaction is used in the separation of benzoic acid, and also in separating iron from manganese.

Uses.—Benzoic acid is used in medicine; but for this purpose only the natural product, obtained from gum benzoin by sublimation, is suitable. Adulteration with the artificial acid is detected by heating a portion of the acid on platinum wire and holding a porcelain dish moistened with phloroglucolvanillin over the flame; the production of a red colour, due to the presence of hydrochloric acid, indicates the presence of the artificial acid. Artificial benzoic acid is employed in the manufacture of aniline blue. It has been used as a mordant in calico-printing. Benzoic acid, dissolved in a mixture of 1 part of ether and 20 parts of alcohol, has been recommended for the preservation of anatomical preparations. It is said to be used in giving an aroma to tobacco.

As an antiseptic it is injurious to health, producing serious disturbance of the metabolic functions, attended with injury to the digestion (Wiley, U.S. Dept. of Agric., J. Soc. Chem. Ind. 1908, 914).

For its use as an acidimetric standard, *see* Morey, J. Amer. Chem. Soc. 1912, 34, 1027; Analyst, 1912, 458.

Detection in foodstuffs.—By the production of diaminobenzoic acid (Mohler, Bull. Soc. chim. 3, 414); by the action of the acid on rosaniline hydrochloride dissolved in aniline oil, when aniline blue is formed (De Brevans, J. Pharm. Chim. 14, 438); by converting the acid into salicylic acid with hydrogen peroxide, and then adding ferric chloride (Jonescu, J. Pharm. Chim. 29, 523). *In butter*: By the formation of ammonium diaminobenzoate, which gives a brownish-red colouration in alkaline solution (Halphen, Pharm. J. 28, 201; Robin, Ann. Chim. anal. 14, 53). *In fermented beverages and milk*: As in butter (Robin, Ann. Chim. anal. 14, 53; Breustedt, Arch. Pharm. 237, 170). *In meats and fats* (Fischer and Gruenert, J. Soc. Chem. Ind. 28, 849).

Examination of the commercial product.—The artificial benzoic acid of commerce is almost always contaminated with chlorobenzoic acids (*v. supra*), the presence of which in any considerable quantity is stated to be detrimental in the aniline blue manufacture. The chlorine may be detected by heating the acid with metallic sodium, extracting the residue with water and testing the solution with silver nitrate. The acid should have the proper melting-point, and should dissolve without residue in boiling water.

Salts and esters of benzoic acids. Benzoic acid is monobasic. Most of the benzoates are soluble both in water and in alcohol. *Potassium benzoate* $C_7H_5O_2K,3H_2O$: efflorescent laminæ. *Sodium benzoate* $C_7H_5O_2Na,H_2O$: efflorescent needles, used for inhalation in tuberculosis. *Ammonium benzoate* $C_7H_5O_2(NH_4)$, rhombic crystals, also used in medicine. *Calcium benzoate* $(C_7H_5O_2)_2Ca,3H_2O$, lustrous needles, used in the preparation of benzophenone. Other hydrates are known. Forms an unstable dialcoholate. *Basic ferric benzoate*

$$(C_7H_5O_2)_2Fe,Fe(OH)_2$$

(*v. supra*). *Mercuric benzoate* small white odourless tasteless crystals; powerful antiseptic; successfully employed in syphilitic and similar diseases (Merck's Bull. 1890, [5] 33; [6] 49; [7] 73).

The esters of benzoic acid are obtained either by distilling benzoic acid with the alcohol and sulphuric acid, or, better, by saturating a solution of benzoic acid in the alcohol with hydrogen chloride, digesting the mixture on the water-bath for some hours, precipitating the ester with water, and purifying by distillation. *Methyl benzoate* $C_7H_5O_2{\cdot}CH_3$ is a liquid boiling at 198·6° (Perkin, Chem. Soc. Trans. 69, 1025). *Ethyl benzoate* $C_7H_5O_2{\cdot}C_2H_5$, boils at 211·8° (Perkin, *l.c.*). *Propyl benzoate* $C_7H_5O_2{\cdot}C_3H_7$, boils at 230·7° (Perkin, *l.c.*).

Benzyl benzoate. This ester forms the therapeutically active portion of Peru balsam, and also the larger fraction of the product formerly known by the name of *cinnamein*, and generally described as consisting chiefly or entirely of benzyl cinnamate. Benzyl benzoate is a colourless oil, boiling at 173° under 9 mm. pressure, whilst the benzyl cinnamate is crystalline, melting at 37°, and boiling at 213°–214° under 9 mm. pressure. It is stated that benzyl benzoate is as efficacious, therapeutically, as the ester obtained direct from Peru balsam, whilst it has the advantages that it is free from colour and smell, is constant in composition, and does not cause the irritation sometimes occasioned by Peru balsam owing to the free acids present (E. Erdmann, Pharm J. 65, 387).

Substitution Derivatives of Benzoic Acid.—*o-Chlorobenzoic acid* $Cl{\cdot}C_6H_4{\cdot}COOH$ melts at 140°, and is obtained by the oxidation of *o*-chlorotoluene. The chlorine atom in this acid is very easily replaceable (Ullmann, Annalen, 1907, 355, 312). The *m*-acid melts at 150°, the *p*- acid at 243°. Nitration of benzoic acid yields mainly the *m*-acid, the relative proportions of the *o*-, *m*-, and *p*-acids formed at different temperatures being shown in the subjoined table (Holleman, Zeitsch. physikal. Chem. 31, 79):

	o.	*m.*	*p.*
−30° . .	14·4	85·0	0·6
0° . .	18·5	80·2	1·3
+30° . .	22·3	76·5	1·2

The *o*-acid, melting at 144°, is prepared by oxidising *o*-nitrotoluene with potassium permanganate, or with manganese dioxide and sulphuric acid (D. R. P. 179589). The *m*-acid, by the action of sodium nitrate and sulphuric acid on benzoic acid, or by oxidising *m*-nitrobenzaldehyde with sodium hypochloride (Badische, Anilin u. Soda Fabrik, D. R. P. 211959). It melts at 140°–141°. The *p*-acid, melting at 238°, is obtained by the oxidation of *p*-nitrotoluene with chromic and sulphuric acids.

Sulphobenzoic acids. The *o*-acid

$$HOOC{\cdot}C_6H_4{\cdot}SO_3H,3H_2O$$

is obtained by the oxidation of toluene-*o*-sulphonic acid, or of thiosalicylic acid, or by diazotising anthranilic acid and adding sulphurous acid. It melts at 68°–69°, and in the anhydrous condition at 134°. Direct sulphonation of benzoic acid yields chiefly the *m*-acid.

BENZOIC ANHYDRIDE $(C_6H_5{\cdot}CO)_2O$. First prepared by Gerhardt (Ann. Chim. Phys. [3] 37, 299) by the action of benzoyl chloride on sodium benzoate or on sodium oxalate, or of phosphorus oxychloride on sodium benzoate:

$$C_6H_5{\cdot}CO_2Na+C_6H_5{\cdot}COCl=(C_6H_5{\cdot}CO)_2O+NaCl;$$

$$2C_6H_5{\cdot}COCl+Na_2C_2O_4 =(C_6H_5{\cdot}CO)_2O+2NaCl+CO+CO_2;$$

$$4C_6H_5{\cdot}CO_2Na+POCl_3 =2(C_6H_5{\cdot}CO)_2O+NaPO_3+3NaCl$$

Preparation.—Pour 100 grams of phosphorus oxychloride over 500 grams of dry sodium benzoate contained in a flask; complete the reaction by heating at 150°; remove sodium salts by washing the cooled mass with dilute sodium carbonate, and purify the anhydride by distillation.

Anschütz (Annalen, 226, 15) heats benzoyl chloride with anhydrous oxalic acid. This avoids the formation of metallic salts altogether.

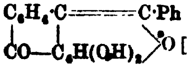
It may also be prepared by heating benzoyl chloride with fused and powdered sodium nitrite for 12 hours; the product is extracted with ether and freed from traces of benzoic acid by rapidly washing with a very dilute solution of sodium carbonate, and finally with distilled water; yield 70 p.c. (Minunni and Caberti, Gazz. chim. ital. 20, 655). By mixing together benzoyl chloride and pyridine and adding water after half an hour, pure benzoic anhydride is precipitated; yield 80 p.c. (Minunni, Gazz. chim. ital. 22, ii. 213). By treating benzoyl chloride with sodium carbonate and pyridine; yield quantitative (Deninger, J. pr. Chem. 50, ii. 479). By treating benzoyl chloride with sodium hyposulphite in the presence or absence of pyridine (Binz and Marx, Ber. 40, 3855); by treating benzenesulphonic chloride with sodium benzoate (Chem. Fab. von Heyden, D. R. P. 123052; Chem. Zentr. 1902, 2, 518); by treating benzoic acid or sodium benzoate with methylchlorsulphate (Bad. Anil. und Sod. Fabrik, D. R. P. 146690; Chem. Zentr. 1904, i. 65); by treating benzoic acid with acetic anhydride in the presence of an indifferent solvent such as benzene or xylene (Kaufmann and Luterbacher, Ber. 42, 3483); from benzotrichloride and acetic acid (Béhal, Compt. rend. 148, 648); by the action of concentrated sulphuric acid on benzotrichloride; and by the action of sulphuryl chloride on a mixture of sodium and calcium benzoates (D. R. P. 161882).

Properties.—Rhombic prisms, sp.gr. 1·1989 15°/4°, melting at 42°, and boiling at 360° (corr.) (Lumsden, Chem. Soc. Trans. 1905, 93). Insoluble in water; readily soluble in alcohol and ether.

Reactions.—Water decomposes it very slowly in the cold, more rapidly on boiling, with formation of benzoic acid. Towards ammonia, amino- and imino- compounds, alcohols and phenols, it behaves like benzoyl chloride, replacing by a benzoyl- group a hydrogen atom attached to nitrogen or oxygen. For this reason it is, like benzoyl chloride (*q.v.*), used as a reagent for amino-, imino, and hydroxyl- groups, and it has the advantage over the latter reagent that no hydrochloric acid, a substance which has a very prejudicial effect on many organic compounds, is liberated during its action.

BENZOÏN GUM *v.* BALSAMS.

BENZOÏN YELLOW. This compound is obtained by condensing benzoin with gallic acid. Benzoïn is added to a solution of gallic acid in sulphuric acid, kept at a temperature of 0°–5°, and, after being stirred during 24 hours, the mixture is poured into water, the dye being precipitated. It crystallises from a mixture of acetic acid and alcohol in yellow needles. Its constitution is given as



$$\begin{array}{l} C_6H_4{\cdot}C \!=\!=\!=\!=\! C{\cdot}Ph \\ \quad | \qquad | \\ CO\!-\!C_6H(OH)_2\!>\!O \end{array}$$

[O : (OH)$_2$: CO = 1 : 2 : 3 : 4] (Bad. Anil. Sod. Fab. D. R. P. 95739; Chem. Zentr. 1898, i. 870, and Graebe, Ber. 31, 2975) (*v.* ALIZARIN AND ALLIED COLOURING MATTERS).

BENZONAPHTHOL, β-NAPHTHOL BENZOATE *v.* SYNTHETIC DRUGS.

BENZOPHENONE (*Diphenyl Ketone*) (*v.* KETONES).

BENZO-QUINONE. *See* QUINONE.

BENZOSALIN. Trade name for benzoyl-salicylic-acid-methyl ester, used in the treatment of articular and muscular rheumatism, neuritis, neuralgia, and sciatica. *V.* SYNTHETIC DRUGS.

BENZOSOL GUIACOL BENZOATE *v.* SYNTHETIC DRUGS.

BENZOTRICHLORIDE *v.* TOLUENE, CHLORINE DERIVATIVES OF.

BENZOYL CHLORIDE $C_6H_5{\cdot}COCl$. First obtained by Liebig and Wöhler, by passing chlorine into benzaldehyde (Annalen, 3, 262). By the action of phosphorus pentachloride on benzoic acid (Cahours, Ann. Chim. Phys. [3] 23, 334).

Preparation.—Benzoic acid is heated with slightly more than the molecular proportion of phosphorus pentachloride

$$C_6H_5{\cdot}COOH + PCl_5 = C_6H_5{\cdot}COCl + POCl_3 + HCl$$

The resulting benzoyl chloride is freed from the phosphorus oxychloride by fractional distillation. Commercial benzoyl chloride is usually contaminated with chlorbenzoylchloride and frequently with small quantities of benzaldehyde (V. Meyer, Ber. 24, 4251, and 25, 209).

From oxalyl chloride, benzene, and aluminium chloride (Staudinger, Ber. 1908, 3566). From benzoic acid or sodium benzoate and methylchlorosulphate (Bad. Anil. und Sod. Fabrik, D. R. P. 146690; Chem. Zentr. 1904, i. 65).

From salts of benzoic acid. By treatment with sulphur dioxide and chlorine (Farb. vorm. Meister, Lucius and Bruning, D. R. P. 210805; Chem. Zentr. 1909, 279); or with sodium chlorosulphonate (D. R. P. 146690); or by the action of sulphuryl chloride on benzoic acid.

Properties.—Colourless liquid, with a pungent odour, boiling at 199° (Lumsden, Chem. Soc. Trans. 1905, 94); 197·2° (corr.) (Perkin, Chem. Soc. Trans. 69, 1244). Its vapour attacks the eyes, causing a flow of tears. Sp.gr. 1·2122 20°/4° (Bruhl, Annalen, 235, 11).

Reactions.—Benzoyl chloride reacts with *water*, slowly in the cold, rapidly on heating, with formation of benzoic and hydrochloric acids. With *ammonia* it forms benzamide

$$C_6H_5{\cdot}CO{\cdot}NH_2$$

together with ammonium chloride. In like manner it reacts with compounds containing hydroxyl-, amino-, or imino- groups, introducing benzoyl in place of hydrogen, and is therefore employed in organic chemistry as a test for the presence of those groups in a compound. Thus with *alcohol* it yields ethyl benzoate; with *aniline*, benzanilide and dibenzanilide.

BENZOYL ECGONINE *v.* COCAINE AND THE COCA ALALOIDS.

BENZOYL FORMIC ACID *v.* KETONES.

BENZOYL GLYCOCOLL *v.* HIPPURIC ACID.

BENZOYL PINK *v.* AZO- COLOURING MATTERS.

BENZOYL SULPHONIC IMIDE and **BENZOIC SULPHIDE** *v.* SACCHARIN.

BENZYLAMINE CARBOXYLIC ACIDS *v.* AMINO-ACIDS (aromatic).

BENZYL BLUE. A dye made by the Aktiengesellschaft für Anilinfabrikation, Berlin, by substituting three atoms of hydrogen in rosaniline by three benzyl-groups. It is easily soluble in water; dyes silks, wools, and cotton (Reimann's Färber-Zeit. 1879, 251; Industrie-Blätter, 39, 360).

BENZYL CHLORIDE *v.* TOLUENE, CHLORINE DERIVATIVES OF.

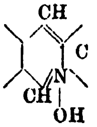
BENZYLDIPHENYLAMINE *v.* DIPHENYLAMINE.

BENZYLMORPHINE *v.* OPIUM.

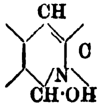
BENZYLPHENYLHYDRAZONES *v.* HYDRAZONES.

BERBERINE AND THE BERBERIS ALKALOIDS. Berberine $C_{20}H_{19}O_5N$ is contained in various species of *Berberis*, especially *B. vulgaris* (Linn.) (the barberry), which also contains berbamine $C_{18}H_{19}O_3N$ (Hesse, Ber. 1886, 19, 3193), and oxyacanthine (*v. infra*), in *Hydrastis canadensis* (Linn.), together with hydrastine and canadine in *Coptis Teeta* (Wall.), which contains as much as 8 p.c., and in many other plants, but not in calumba root (Gordin, Arch. Pharm. 1902, 240, 146).

Preparation.—The best available material from which to extract berberine is the root of *Hydrastis canadensis* (Linn.) ('Golden Seal'), which contains about 4 p.c. of the alkaloid. The finely-powdered hydrastis root is exhausted with alcohol, the greater part of the alcohol removed by distillation, and the alkaloid converted into sulphate or nitrate by the addition of sufficient dilute sulphuric acid or nitric acid. The crude berberine salt which separates is collected, dissolved in water, and mixed with acetone and sodium hydroxide, when the crystalline condensation product, anhydroberberineacetone, separates (Gaze, Zeit. Naturwiss. Halle, 1890, 62, 399). After recrystallisation, this product melts at 175° (corr.) (Pyman, Chem. Soc. Trans. 1911, 99, 1690); it yields with hot dilute mineral acids the corresponding berberinium salts. The free base exists in two isomeric forms, represented by the partial formulæ below:



I.



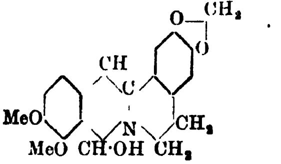
II.

as the quaternary ammonium hydroxide, berberinium hydroxide (I.), which is known only in aqueous solution, and as the carbinolamine, berberine (II.), also termed berberinal and berberinol. For the nomenclature of berberine and its salts, see Perkin (Chem. Soc. Trans. 1918, 113, 503). A solution of berberinium hydroxide is prepared by adding the equivalent quantity of barium hydroxide to an aqueous solution of berberinium sulphate, whilst the addition of an excess of sodium hydroxide to this solution affords a precipitate of the carbinolamine, berberine, which is extracted by ether, and crystallises on concentrating the solution (Gadamer, Arch. Pharm. 1905, 243, 31).

Properties.—Berberine $C_{20}H_{19}O_5N$ crystallises from ether in yellow needles, which melt at 144°, and are anhydrous. It is insoluble in cold water, but on warming gradually yields a solution of berberinium hydroxide. It dissolves in acids, giving salts of berberinium hydroxide. The berberinium salts $C_{20}H_{18}O_4NX$ (where X is a monobasic acid radical) crystallise well, and are of a yellow or red colour. They are sparingly soluble in water, especially in the presence of mineral acids or salts. Their aqueous solutions are neutral to litmus, optically inactive, and have a bitter taste. Berberine is not poisonous to man, and is used medicinally, like preparations of the plants containing it, as a tonic.

Detection and Estimation.—Chlorine water gives with a solution of the hydroxide a bright-red colouration even in very dilute solutions. For the detection of berberine in plants, *see* Gordin, Arch. Pharm. 1902, 240, 146. The same author recommends for its estimation the precipitation of the alkaloid as sulphate from its alcoholic solution, the decomposition of the sulphate by potassium iodide and the titration of the sulphuric acid liberated by means of *N*/40 potassium hydroxide (*ibid.* 1901, 239, 638).

Constitution.—The main features of the constitution of berberine were determined by Perkin (Chem. Soc. Trans. 1889, 55, 63; 1890, 57, 992) by a study of its oxidation products, and subsequent work by Gadamer (Chem. Zeit. 1902, 26, 291, 385; Arch. Pharm. 1905, 243, 31; 1910, 248, 43), Perkin and Robinson (Chem. Soc. Trans. 1910, 97, 321), and Tinkler (*ibid.* 1911, 99, 1340), established the formula given below, which has since been confirmed through the synthesis of the alkaloid by Pictet and Gams (Ber. 1911, 44, 2480).



Attention may be drawn to the similarity between the formula of berberine and that of hydrastine which occurs with it in *Hydrastis canadensis* (Linn.).

Oxycanthine $C_{19}H_{21}O_3N$ accompanies berberine in *Berberis vulgaris* (Linn.) (Polex, Arch. Pharm. 1836, [ii.] 6, 271; Hesse, Ber. 1886, 19, 3190; Rüdel, Arch. Pharm. 1891, 229, 631), and may be isolated from the mother-liquor from which all the berberine salt has crystallised by precipitation with sodium carbonate. It crystallises with difficulty from alcohol or ether, m.p. 208°–214° (Hesse), is insoluble in water, easily soluble in chloroform, less so in alcohol. The alcoholic solution is dextrorotatory, and has a bitter taste. It yields crystalline salts

F. L. P.

BERENGELITE. A bituminous resinous mineral from San Juan de Berengela, melting at 100°, soluble in alcohol and ether. According to Dietrich, specimens from Trinidad and Arica, Chile, contained 71·84 C, 9·95 H, and 18·21 of O (Chem. Zentr. 80, 559). Used for caulking ships.

BERGAMOT *v.* OILS, ESSENTIAL.

BERGMANN'S POWDER. An explosive composed of 50 parts potassium chlorate, 5 of pyrolusite, and 45 of bran, sawdust, or tan (J. 37, 1748).

BERLIN BLACK. A black varnish drying with a dead surface, used for coating ironwork.

BERLIN BLUE or **PRUSSIAN BLUE** *v.* CYANIDES.

BERNTHSEN'S VIOLET. *Isothionine. β-Amidothiodiphenylimide.* Formed by reducing β-dinitrodiphenylaminesulphoxide and oxidising the leuco- base with ferric chloride. The hydrochloride crystallises in needles. Dyes reddish-violet. Isomeric with *Lauth's violet* (Bernthsen, Annalen, 230, 133).

BERRY WAX *v.* WAXES.

BERTHIERINE *v.* THURINGITE.

BERTHIERITE. *Iron sulphantimonite* (*v.* ANTIMONY).

BERYL. A mineral consisting of glucinum aluminium silicate $Gl_3Al_2Si_6O_{18}$, crystallising in the hexagonal system. The ancient name, βήρυλλος, included also some other gem-stones of a greenish colour. The crystals are usually quite simple in form, with only the hexagonal prism and the basal plane; the habit being commonly prismatic and the prism faces striated vertically. They are usually cloudy or opaque, with a pale-greenish or yellowish colour and are often of considerable size, crystals weighing as much as one or two tons having been found at Acworth in New Hampshire. The sp.gr. is 2·63–2·80, and the hardness 7½–8. The material is not attacked by acids, except hydrofluoric; and before the blowpipe is fusible only with difficulty on the edges.

Crystals of a different type are found in association with lithia minerals (lepidolite and rubellite) in pegmatites in the Urals, California, and Madagascar. These are tabular in habit and rose-red or colourless. Further, they differ chemically in containing small amounts of alkalis (Cs_2O 3·1, Li_2O 1·4 p.c.). V. Vernadsky (1908) expresses the composition by the formula $x GlAl_2Si_4O_{12} \cdot yA$, where A is GlH_2SiO_4, $GlSiO_3$(?), Cs_2SiO_3, Li_2SiO_3, or Na_2SiO_3; and for the cæsium-bearing variety he proposes the name *vorobyevite*.

Being by far the most abundant of glucinum minerals, beryl is employed for the preparation of the little-used salts of glucinum. It finds more extensive application in jewellery. The clear grass-green variety is the *emerald*, one of the most valuable of gems on account of the rarity of flawless material. Gem-stones of a greenish, bluish, or sea-green colour are known as *aquamarine*. Pink beryl of gem quality has been called *morganite*, and a golden beryl from South-West Africa is given the name *heliodor*. For a fuller description of material of gem quality and its occurrences, *see* M. Bauer, Precious Stones, transl. by L. J. Spencer, London, 1904. On the gem beryls from Madagascar, *see* A. Lacroix, Minéralogie de la France, 1910, 1913. L. J. S.

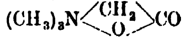
BERYLLIUM *v.* GLUCINUM.

BERZELIANITE. Native copper selenide Cu_2Se, occurring in a black powdery form in calcite at Skrikerum in Sweden and at Lehrbach in the Harz. Named after the Swedish chemist J. J. Berzelius (1779–1848), who first analysed it. L. J. S.

BERZELITE. Arsenate of calcium, manganese, and magnesium $(Ca,Mn,Mg)_3As_2O_8$, occurring as small yellow cubic crystals, and as compact masses, with ores of iron and manganese at Långban in Wermland, Sweden. Also named after J. J. Berzelius. Other forms of the same name, berzeline and berzelite, have been applied to these, as well as to some other minerals. L. J. S.

BESSEMER STEEL *v.* IRON.

BETAFITE. The betafite group of minerals, recognised by A. Lacroix in 1912 in the pegmatites of Madagascar, includes betafite, samiresite, and blomstrandite (of G. Lindström, 1874). They are titano-columbates (and tantalates) of uranium, &c., crystallising in the cubic system, and closely allied to pyrochlore and hatchettolite. From the former they differ in containing only little lime and rare-earths and an absence of alkalis and fluorine; and from the latter in containing titanium. Betafite is a hydrated titano-columbate of uranium (UO_3 26–28 p.c.). Sharply developed octahedral crystals with the edges truncated by faces of the rhombic-dodecahedron have been found in considerable numbers at Ambolotara near Betafo, and other localities in Madagascar. They reach an inch in diameter, and show a dull yellow weathered surface, but in the interior the material is brownish-black with a bright greasy lustre. Sp.gr. 3·59–4·475 depending on the degree of hydration. Samiresite, a titano-columbate of uranium (UO_3 21 p.c.) and lead, is from Samiresy near Antsirabe. In blomstrandite a part of the columbium is replaced by tantalum. (A. Lacroix, Minéralogie de la France et de ses colonies, 1913, vol. v.) L. J. S.



BETAINE $(CH_3)_3N\left\langle\begin{matrix}CH_2\\O\end{matrix}\right\rangle CO$ may be regarded as the internal anhydride of the acid $(CH_3)_3N(OH) \cdot CH_2 \cdot COOH$ derived from acetic acid by the replacement of one atom of hydrogen by trimethyl hydroxyammonium. It occurs in beets and mangolds (especially unripe roots), in cotton seed, in the shoots of barley, in wormseed (*Artemisia gallica*) and in many other plants, often in association with choline, from which it may readily be obtained by oxidation. For observations on the localisation of betaine in plants and its part in the nitrogen metabolism, *see* Stanĕk (Zeitsch. physiol. Chem. 1911, 72, 402). Betaine is found in the extracts of muscles from the scallop, periwinkle, and lamprey.

Betaine can be synthesised by the interaction of chloracetic acid and trimethylamine (Liebreich, Ber. 1869, 2, 13). It can also be obtained by the action of a methyl haloid upon methyl dimethylaminoacetate (J. Chem. Soc. Abst. 1914, 1, 938).

It can be extracted from beet-root molasses by dilution with water, boiling with baryta, filtering, precipitating the excess of BaH_2O_2 with CO_2, evaporating the liquid to small volume, and extracting with alcohol. The alcoholic solution is treated with alcoholic zinc chloride, the ppt. recrystallised from water and decomposed by baryta water. The barium is then exactly removed from the filtrate by H_2SO_4, and betaine hydrochloride crystallises on evaporation (Liebreich, Ber. 3, 161; Frühling and Schulz. Ber. 10, 1070).

Urban (Zeitsch. Zuckerind. Bohm. 1913, 37, 339) gives the following method. The evaporated molasses residues are mixed with an equal volume of concentrated hydrochloric acid. After cooling, the alkali chlorides which have separated are removed by filtration, and the filtrate is evaporated. The volatile organic acids and hydrochloric acid pass away, and humus substances are precipitated. These are also filtered off, and the residue further evaporated to a thick syrup. This is dissolved in water, filtered, decolourised by charcoal, and concentrated, when nearly pure betaine hydrochloride separates out (*cf.* Ehrlich, Ber. 1912, 45, 2409; also Andrlik, Z. Zuckerind, Bohm. 1915, 39, 387; J. Soc. Chem. Ind. 1915, i. 781; J. Soc. Chem. Ind. 1915, 1064).

A general method of obtaining betaine from plant extracts is to precipitate with lead acetate, filter, remove the lead by sulphuretted hydrogen, filter, evaporate to dryness, extract residue with alcohol, and precipitate with alcoholic mercuric chloride. The mercuric double salt is then recrystallised, decomposed by sulphuretted hydrogen, and the hydrochloride obtained from the solution by evaporation. If choline is also present, it can be removed from the mixed hydrochlorides by extraction with cold alcohol, leaving the betaine hydrochloride (Schulze, Zeitsch. physiol. Chem. 1909, 60, 155).

Betaine crystallises from alcohol in large crystals containing one molecule of water. It is deliquescent in air, and loses its water when dried over sulphuric acid. Strong sulphuric acid has but little action upon it, even at 120° (Staněk, Zeit. Zuckerind, Bohm, 1902, 26, 287).

It is neutral to litmus, and has a sweet taste. It melts and decomposes at 293° (Willstatter, Ber. 1902, 35, 584), giving off the smell of trimethylamine and of burnt sugar. The aurichloride $C_5H_{11}NO_2\cdot HCl\cdot AuCl_4$, forms plates or needles which melt at 209° (Willstatter), or, according to Fischer (Ber. 1902, 35, 1593), at 250°. The platinichloride $PtCl_4 2(C_5H_{11}NO_2, HCl), 4H_2O$ forms large plates; after losing its water it melts and decomposes at 242° (Willstatter).

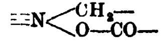
$C_5H_{11}NO_2\cdot HCl$ is very soluble in water, slightly soluble in cold alcohol. $C_5H_{11}NO_2\cdot HI$ is soluble in water or boiling alcohol, and melts at 188°–190°. A compound with KI crystallises as $(C_5H_{11}NO_2)_2\cdot KI, 2H_2O$, m.p. 139° (Korner and Menozzi, Gazz. chim. ital. 13, 351), or, if anhydrous, at 228°–229° (Willstatter).

Stoltzenberg (Zeitsch. physiol. Chem. 1914, 92, 445) prepared the following compounds of betaine:—

The hydrofluoride and acid hydrofluoride, basic hydrochloride $(C_5H_{11}NO_2)_2HCl\cdot H_2O$, monoclinic prisms, m.p. 250° (decomp.); $C_5H_{11}NO_2\cdot HBr$, m.p. 233° (decomp.); basic hydrobromide $(C_5H_{11}NO_2)_2HBr$, prisms, m.p. 262°; basic hydriodide $(C_5H_{11}NO_2)_2HI$, glittering plates, m.p. 242°; basic aurichloride $5C_5H_{11}NO_2\cdot 4AuCl_4\cdot H_2O$, yellow crystalline powder, m.p. 169° (decomp.); basic auribromide $5C_5H_{11}NO_2\cdot 4AuBr_4$, m.p. 185°; auribromide $C_5H_{11}NO_2\cdot HAuBr_4$, dark brown plates, m.p. 260° (decomp.); two platinichlorides, one with $4H_2O$, m.p. 254°–255°, the other with $3H_2O$, m.p. 255°–260°; a basic platinichloride $5C_5H_{11}NO_2\cdot 4H_2PtCl_6$, orange crystals, m.p. 246° (decomp.); the phosphate, m.p. 199°; the sulphate $(C_5H_{11}NO_2)_2H_2SO_4$, rhombic crystals, m.p. 180°; the nitrate, m.p. 124°; the chlorate, m.p. 115° the dichromate, m.p. 226°–227° (decomp.) and the permanganate, m.p. 120°. The chlorate and permanganate explode on percussion or rapid heating.

On heating betaine with potassium hydroxide at 200°–220°, about one-third of the nitrogen is eliminated as trimethylamine, carbon dioxide being evolved. The compound in alkaline solution gives a *hydrochloride* $C_4H_9O_2N,HCl$, m.p. 187°–189°. The platinochloride forms a yellow crystalline mass, m.p. 120°–121° (Albers, Chem. Zeit. 1913, 37, 1533).

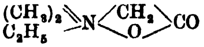
The term 'betaine' is now generally used for substances containing the group



$$\equiv N{<}\begin{matrix}CH_2-\\O-CO-\end{matrix}$$

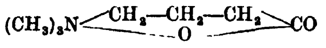
with other alkyl- groups than methyl, or other acyl- groups than acetyl.

Thus, *dimethylethylacetylbetaine* or (since acetyl is to be understood if no acyl- group is mentioned) *dimethylethylbetaine*



$$\begin{matrix}(CH_3)_2\\C_2H_5\end{matrix}{>}N{<}\begin{matrix}CH_2\\O\end{matrix}{>}CO$$

crystallises from alcohol in four-sided plates, melting and decomposing at 229°–231° (Willstatter), while *trimethylbutyrobetaine*



$$(CH_3)_3N{<}\begin{matrix}CH_2-CH_2-CH_2\\O\end{matrix}{>}CO$$

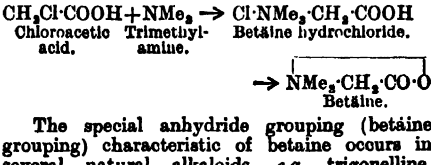
crystallises in colourless plates with $3H_2O$; in the anhydrous state it softens at 130° and decomposes at 222° (Willstatter).

The betaines are isomeric with the esters of amino- acids; thus, ordinary betaine is isomeric with methyldimethylaminoacetate $(CH_3)_2N\cdot CH_2\cdot CO\cdot OCH_3$, a volatile oily liquid, b.p. 135°, while trimethylbutyrobetaine is isomeric with methyl-γ-dimethylaminobutyrate $(CH_3)_2:N\cdot CH_2\cdot CH_2\cdot CH_2\cdot COO\cdot CH_3$, b.p. 171°–173°.

(For betaines of the pyridine series, *see* Kirpal, Monatsh. 1908, 29, 471).

According to Schulze and Trier (Zeitsch. physiol. Chem. 1910, 67, 46), the three betaines which have been isolated from plant tissues are: betaine, trigonelline [found in fenugreek by Jahns (Ber. 1885, 18, 2518) associated with choline], and stachydrine, found in the tubers of *Stachys tuberifera* and in the leaves of *Citrus aurantium* (*v.* TRIGONELLINE and STACHYDRINE).

Betäine $C_5H_{11}O_2N$ (*lycine, oxynevrine*) occurs in sugar-beet and in numerous other plants. Crystalline, m.p. 293° (dry), optically inactive. Sweet taste. The hydrochloride has been used in medicine. It is formed by the oxidation of choline and by the action of trimethylamine on chloroacetic acid

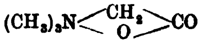


$$\underset{\text{Chloroacetic acid.}}{CH_2Cl\cdot COOH}+\underset{\text{Trimethylamine.}}{NMe_3}\rightarrow\underset{\text{Betäine hydrochloride.}}{Cl\cdot NMe_3\cdot CH_2\cdot COOH}$$

$$\rightarrow\underset{\text{Betäine.}}{\overbrace{NMe_3\cdot CH_2\cdot CO\cdot O}}$$

The special anhydride grouping (betäine grouping) characteristic of betaine occurs in several natural alkaloids, *e.g.* trigonelline. Naturally occurring betäines of other amino-acids are betonicine, ergothioneine, hypaphorine, trimethylhistidine, trigonelline, and stachydrine. *See* Barger, The Simpler Natural Bases, chap iii., Longmans, 1914. H. I.

BETAINES are completely methylated amino-acids with quinquevalent nitrogen. Bases of this type derived from several of the amino-acids of protein occur naturally in plants and animals. *Betaine* par excellence



$$(\mathrm{CH_3})_3\mathrm{N}<\begin{matrix}\mathrm{CH_2}\\ \mathrm{O}\end{matrix}>\mathrm{CO}$$

is the most important and the simplest, being trimethylglycine, and later gave its name to the whole class (for the nomenclature and general properties of which, *see* Willstatter, Ber. 1902, 35, 584, and S. Komatsu, Mem. Coll. Sci. Kyoto, 1916, 1, 369). Betaine (acetobetaine, oxyneurine, lycine) occurs in *Beta vulgaris*, the sugar-beet, and in all other *Chenopodiaceæ* examined, sporadically in a number of other plants, in mussels, cuttle fish, crayfish, &c. For localisation and migration of betaine in plants, *see* Stanék (Zeitsch. physiol. Chem. 1911, 72, 402 and Zeit. Zuckerind, Böhm. 1916, 40, 300). Young sugar beets contain more than older ones. Crude beet-sugar may contain 0·375 p.c. of betaine (Waller and Plimmer, Proc. Roy. Soc. 1903, 72, 345). The only practical natural source is the final mother liquor left after desaccharification of the molasses by strontium, which liquor, with 20 p.c. of water, may contain 115 grams of betaine per kilo. The extraction of betaine is apparently best carried out by vigorous agitation with 96 p.c. alcohol. After evaporation of the alcohol the betaine is converted into chloride and crystallised as such. Yield of the liquor of pure chloride 10–12 p.c. of the liquor employed (Ehrlich, Ber. 1912, 45, 2409; D. R. P. 157173; *cf.* Stoltzenberg, Ber. 1912, 45, 2248; D. R. P. 243332; and Chem. Zentr. 1914, i. 22; Urban, Zeit. Zuckerind. Böhm. 1913, 37, 339; Andrlik, *ibid.* 1915, 39, 387).

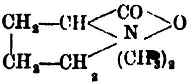
Betaine is also obtained by the oxidation of choline ('oxyneurine,' Liebreich, 1869), by the methylation of glycine and, as chloride, by the action of trimethylamine on chloracetic acid. A synthesis by heating methyldimethylaminoacetate with methyl halides and subsequent hydrolysis of the betaine ester with acids is stated to give a quantitative yield, and has been patented (D. R. P. 269338). For the isolation from plant extracts (Schulze) and estimation (Stanék), *see* the article on Choline.

Betaine crystallises from alcohol in deliquescent crystals, which lose one molecule of water at 100°, presumably changing from the ammonium hydroxide to the cyclic anhydride. It melts at 293° with partial isomerisation to methyldimethylaminoacetate (Willstatter, *l.c.*). It is a very feeble base, and neutral to litmus. The *chloride* $\mathrm{Cl(CH_3)_3N{\cdot}CH_2{\cdot}COOH}$ forms leaflets very soluble in water, and peculiar among the chlorides of organic bases in being hardly soluble in alcohol (1 part in 365 c.c. at room temperatures; separation from choline and other bases). This salt has a strongly acid reaction and has been used as a solid substitute for hydrochloric acid under the name 'acidol' in the preparation of tablets, &c. (*c.f.* acid pepsin tablets, D. R. P. 172862). When pure it is a convenient standard for alkalimetry. The *aurichloride* $\mathrm{C_5H_{11}O_2N{\cdot}HAuCl_4}$ is the most characteristic derivative, and is dimorphous; regular, m.p. 209°, and rhombic, m.p. 248°–250° (Fischer, Ber. 1902, 35, 1593; Willstätter, *ibid.* 2700). The *platinichloride*

$$(\mathrm{C_5H_{11}O_2N})_2\mathrm{H_2PtCl_6},$$

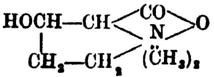
m.p. 242°, crystallises from hot water in anhydrous needles, which in contact with the aqueous mother liquor form four-sided tables with $4\mathrm{H_2O}$ (Trier, Zeitsch. physiol. Chem. 1913, 85, 372), who recommends this as a test for betaine). The *picrate*, m.p. 180°, may also be used for the separation from mixtures. A large number of other salts have been described by Stoltzenberg (Zeitsch. physiol. Chem. 1914, 92, 445). Betaine is not a nitrogenous food; it has no appreciable action on animals, and the part played by it in plant economy is obscure.

Other betaines occurring naturally, are: *Stachydrine*



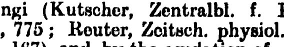
the betaine of α-pyrrolidine carboxylic acid (proline) was discovered in the edible tubers of *Stachys tubifera* (Von Planta, Ber. 1890, 23, 1699), and occurs in a few other plants. According to Yoshimura and Trier (Zeitsch. physiol. Chem. 1912, 77, 290), the alkaloid chrysanthemine described by Marino-Zuco as occurring in Dalmatian insect powder (*Chrysanthemum cinerariaefolium*) is a mixture of stachydrine and choline. Stachydrine has been obtained synthetically by methylating proline (Engeland, Ber. 1909, 42, 2962), and from the methyl ester of hygric acid (Trier, Zeitsch. physiol. Chem. 1910, 67, 324).

Betonicine



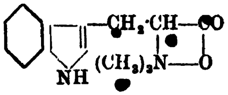
is dextro rotatory oxyproline betaine and *turicine* its stereoisomer. Both occur in *Betonica officinalis* and have been obtained by methylating natural oxyproline (Küng, Zeitsch. physiol. Chem. 1913, 85, 217), and natural 4-hydrohygric acid (Goodson and Clewer, Trans. Chem. Soc. 1919, 115, 923).

Trimethylhistidine



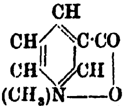
the betaine of histidine, has been obtained from fungi (Kutscher, Zentralbl. f. Physiol. 1910, 24, 775; Reuter, Zeitsch. physiol. Chem. 1912, 78, 167), and by the oxidation of *ergothioneine* (Barger and Ewins, Biochem. J. 1913, 7, 204). The latter base contains an additional sulphur atom in the glyoxaline ring and occurs in ergot (*q.v.*).

Hypaphorine



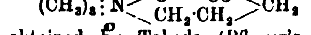
the betaine of tryptophane, occurs in the seeds of *Erythrina Hypaphorus* of Java (Greshoff, Mededeelingen uit's Lands Plantentuin, 1898). For constitution and synthesis, *see* Van Romburgh and Barger, Chem. Soc. Trans. 1911, 99, 2068.

All the above are derived from α-amino-acids. The next three are not. *Trigonelline*



the betaine of nicotinic acid, has been found in quite a number of plants, but generally only in very small amount. It probably occurs in many more species. It was discovered in the fenugreek (*Trigonella fœnum græcum*) by Jahns (Ber. 1885, 18, 2518), who later showed it to be identical with the 'methylbetain' of nicotinic acid, already synthesised by Hantzsch (Ber. 1886, 19, 3140).

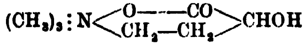
γ-Butyrobetaine



$$(CH_3)_3:N<\begin{matrix}O—CO\\ CH_2\cdot CH_2\end{matrix}>CH_2$$

was obtained by Takeda (Pfluger's Archiv. 1910, 133, 365) from dog's urine after phosphorus poisoning (which interferes with the deaminating action of the liver). It is almost certainly identical with one, if not with three, of Brieger's putrefaction bases (Untersuch. über Ptomaine, i. p. 27, Berlin, 1886), and was first synthesised by Willstätter (Ber. 1902, 35, 584).

Carnitine, α-hydroxy-γ-butyrobetaine



$$(CH_3)_3:N<\begin{matrix}O——CO\\ CH_2—CH_2\end{matrix}>CHOH$$

is a hydroxy derivative of the foregoing, and was isolated from meat extract (yield 1.3 p.c.) by Gulewitsch and Krimberg (Zeitsch. physiol. Chem. 1905, 45, 326), and by Kutscher (Zeit. Unters. Nahr. Genussm. 1905, 10, 528; 'novain'). According to the latter, it is identical with a base $C_7H_{15}O_3N$, isolated from human urine by Dombrowski (Compt. rend. 1902, 135, 244). Heating with baryta yields trimethylamine and crotonic acid; phosphorus and hydriodic acid reduce to γ-butyrobetaine. Racemic carnitine was probably synthesised by Fischer and Göddertz (Ber. 1910, 43, 3272). The small differences from natural carnitine were probably connected with the optical activity of the latter substance.

Myokynine, isolated by Ackermann (Zeit. Biol. 1912, 59, 433) from the muscles of horses and dogs, is probably *l*-hexamethyl-ornithine $(CH_3)_3N(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH\cdot(COOH)\cdot N\cdot(CH_3)_3OH$

All the above bases, or at least all the α-betaines, are without marked physiological activity.

For a fuller account of betaines, *see* Barger, The Simpler Natural Bases, Longmans, 1914.

G. B.

BETEL. A mixture of the leaf of the betel-pepper, *Piper Betle* (Linn.) with the fruit of *Areca catechu* (Linn.) or betel nut and *chunam* (lime obtained by calcining shells), universally used by the people of Central and Tropical Asia as a masticatory.

BETEL-NUT. The fruit of *Areca catechu* (Linn.) *v.* Areca Nut.

BETH-A-BARRA WOOD. A wood imported from the West Coast of Africa, much valued for its toughness and capability of receiving a high polish. The interstices of the fibres are filled with a yellow crystalline substance which can be extracted from the sawdust by heating with distilled water containing a little sodium carbonate, and precipitating the resulting claret-coloured solution with acetic acid. It is purified by repeated crystallisations from 80 p.c. alcohol. By precipitating the red solution with hydrochloric acid and washing the resulting precipitate with ether, Greene and Hooker (Amer. Chem. J. 11, 267) found the crystals to be identical in all respects with lapachic acid.

It differs from chrysophanic acid by melting at 135° and in not forming a compound with alum (Sadtler a. Rowland, Amer. Chem. J. 1881, 22). (For tables showing the difference in the reactions of brasilin, hæmatoxylin, santalin, and beth-a-barra, *v.* Amer. Chem. J. 11, 49, and Wagner's Jahr. 28, 537.)

BETOL β-NAPHTHOL SALICYLATE *v.* Synthetic drugs.

BETONICINE *v.* Betaines.

BETORCIN or **β-ORCIN** $C_8H_{10}O_2$. A substance obtained by the decomposition of barbatic acid, found in the lichen *Usnea barbata.* It is less soluble in water than orcin, and gives a deeper crimson colour with hypochlorites. Kostanecki has obtained it by the action of nitrous acid on *m*-amino-*p*-xylenol, thus showing that it is a dihydroxy-xylene (dimethylresorcinol) having the substituting groups in the positions CH_3, CH_3, OH, OH=1, 4, 3, 5 (Stenhouse a. Groves, Chem. Soc. Trans. 37, 396; Lampartie, Annalen, 134, 248; Menschutkin, Bull. Soc. chim. 2, 428; Kostanecki, Ber. 19, 2321).

BETULA RESIN *v.* Resins.

BETULOL $C_{15}H_{24}O$, a bicyclic sesquiterpene alcohol of the terbene type found in birch oil, B.P. 157–°158°/13 mm., D^{16}0·9777, $n\cdot{}^{16}_{D}$1·5150, $a^{16}_{D}-26\cdot5°$. Slowly absorbs hydrogen in presence of platinum yielding *tetrahydrobetrol*, b.p. 153°–158°/14 mm., D^{18} 0·9415, n^{18}_{D} 1·4908, $a^{18}_{D}-6.8°$, and bicyclic *tetrahydrobetulene* $C_{15}H_{28}$, b.p. 118°–120°/11 mm.; D^{18} 0·8737, n^{18}_{D} 1·4744, $a^{18}_{D}-3°$. For other derivatives *see* Semmler, (Jonas and Richter, Ber. 1918, 51, 417).

BEZETTA. *Tournesol en drapeaux. Schminklappchen. Bezetta rubra et cœrulea.* A dye or pigment prepared by dipping linen rags in solutions of certain colouring matters. Red bezetta is coloured with cochineal, and is used as a cosmetic.

Blue bezetta (*Tournesol en drapeaux*), which is chiefly used for colouring the rind of Dutch cheeses, is prepared at Gallargues, near Nîmes, in the department of Gard, from a euphorbiaceous plant, *Chrozophora tinctoria* (A. Juss.) [*Croton tinctorius*]. The fruits and the tops of the plants are gathered, and, the juice being expressed, rags of coarse cloth are dipped into it, then dried, and afterwards exposed to the fumes of mules' or horses' dung. This last operation is called *aluminadou.* The cloths are turned from time to time, to ensure uniform colouration and prevent any part from being exposed too long to the fumes of the dung, which would turn them yellow. They are then dried a second time, again soaked in the juice, mixed this time with urine, and lastly exposed for some time to the action of the sun and wind. The quantity thus manufactured amounts to about 50 tons yearly. The blue of bezetta is reddened by acids like litmus, though not so quickly, but differs from the latter in not being restored by alkalis. According to Joly, the same dye may be obtained from other euphorbiaceous plants, *Chrozorphora oblongata* [*obliqua* (A. Juss.) ?], *C. plicata* (A. Juss.), *Argithamnia tricuspidata* (Muell.), *Mercurialis perennis* (Linn.), and *M. tomentosa* (Linn.). The juice exists in all these plants in the colourless state, and turns blue only on exposure to the air (Handw. d. Chem. 2, [1] 1030; Gerh. Traité, 3, 820).

BEZOAR. This name, which is derived from a Persian word signifying an antidote to poison, was given to a concretion found in the stomach or intestines of an animal of the goat kind, *Capra aegragus*, which was once very highly valued for this imaginary quality, and has thence been extended to all concretions found in animals.

According to Taylor (Phil. Mag. No. 186, 36, and No. 188, 192), bezoars may be divided into nine varieties: 1. Phosphate of calcium, which forms concretions in the intestines of many mammalia. 2. Phosphate of magnesium; semi-transparent and yellowish, and of sp.gr. 2·160. 3. Phosphate of ammonium and magnesium; a concretion of a grey or brown colour, composed of radiations from a centre. 4. Oxalate of calcium. 5. Vegetable fibres. 6. Animal hair. 7. Ambergris. 8. Lithofellic acid. 9. Ellagic or bezoardic acid.

Of true bezoars there are three kinds: Oriental, Occidental, and German. The true Oriental bezoars found in the *Capra ægragus*, the gazelle (*Gazella dorcas*), and other ruminant animals, are spherical or oval masses, varying from the size of a pea to that of the fist, and composed of concentric layers of resinous matter with a nucleus of some foreign substance, such as pieces of bark or other hard vegetable matter which the animal has swallowed. They have a shining resinous fracture, are destitute of taste and odour, nearly insoluble in water and aqueous hydrochloric acid, but soluble for the greater part in potash lye. These characters suffice to distinguish the Oriental bezoars from those varieties which contain a considerable quantity of inorganic matter. There are two kinds of them, the one consisting of ellagic, the other of lithofellic acid. The latter have a more waxy lustre and greener colour than the former, and are also distinguished by their lower sp.gr., viz. 1·1, whilst that of the ellagic acid stones is 1·6. They contain, besides lithofellic acid, a substance resembling the colouring matter of bile, and are perhaps biliary calculi. Oriental bezoars are greatly prized in Persia and other countries of the East for their supposed medical properties. The Shah of Persia sent one in 1808 as a present to Napoleon. The Occidental bezoars are found in the lama (*Auchenia glama*) and in *A. vicugna.* They resemble the Oriental in external appearance, but differ totally in their chemical characters, inasmuch as they consist chiefly of calcium phosphate, with but little organic matter. German bezoars, which are chiefly obtained from the chamois or gemsbock (*Rupicapra tragus*), consist chiefly of interlaced vegetable fibres or animal hairs bound together by a leathery coating.

BICUHYBA FAT. *See* MYRISTICA FAT GROUP.

BIDRY. An Indian alloy of zinc, copper, and lead, and occasionally tin. Articles of this alloy, after being turned in a lathe and engraved, are blackened by immersion in a solution of sal ammoniac, nitre, common salt, and copper sulphate. Known also as *Vidry.*

BIEBRICH ACID RED, PATENT BLACKS, SCARLET PONCEAU *v.* AZO- COLOURING MATTERS.

BIGNONIA TECOMA.[1] **TECOMIN.** The *Bignonia tecoma* is a somewhat common tree in the uplands of Minas, Brazil, which when fully grown is about 30 feet high and in September is covered with brilliant yellow flowers. The natives mix the sawdust and shavings of this tree with slaked lime, heat the mass with water and employ the resulting bath to dye cotton cloth. A paste made of the sawdust mixed with lime is also used to stain lighter-coloured woods a deep brown. By exhausting the sawdust with boiling 85 p.c. alcohol and concentrating the extract, Lee (Chem. Soc. Trans. 1901, 79, 284) isolated the colouring matter *tecomin.* This, which has apparently not been submitted to analysis, forms shining chrome-yellow crystals possessing a nacreous lustre, soluble in alkalis with a rose-red colouration.

A further quantity of this compound could be isolated from the alcoholic filtrate, the total amount thus given by the wood being approximately 5 p.c.

The sawdust extracted with alcohol still contains a deep brown dye which may now be removed from it by alkalis, and by acidification this is deposited as an amorphous brown powder. Nothing is at present known as regards the relationship, if such exists, between tecomin and the colouring matter of chica red or carajura, which originates from the Bignonia chica. A. G. P.

BIKHACONITINE *v.* ACOTININE.

BILBERRY. *Vaccinium Myrtillus* (Linn.). König gives as the average composition of the fruit:

Water	Protein	Free acid	Sugar	Other carbo-hydrates	Crude fibre	Ash
78·4	0 8	1·7	5·0	0·9	12·3	1·0

According to Otto (Bied. Zentr. 1899, 28, 284), Silesian bilberries contain from 3·5 to 7·0 p.c. of sugar and acid corresponding to from 0·9 to 1·5 p.c. of tartaric acid. He found that fermentation of the juice with ordinary yeast was very slow unless some nitrogenous matter (*e.g.* ammonium chloride or, better, asparagine (about 0·6 gram per litre)) were added. Bilberries contain a small quantity of a wax melting at 71° (Seifert, Landw. Versuchs-Stat. 1894, 45, 29).

The juice of bilberries contains from 4 to 9·5 p.c. of total solids, 0·25 to 0·31 p.c. ash, and acidity corresponding to from 15·5 to 19·6 c.c. N/1 alkali. The juice contains some substance which gives a blue colouration when heated with hydrochloric acid. This colouration is apparently not connected with the red colouring matter of the berries and appears to be characteristic of the *Vacciniaceæ* for cranberries, *Vaccinium vitis Idæa* also yield the same reaction (Plahl, Zeitsch. Nahr. Genussm. 1907, 13, 1).

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[1] According to Holmes the name *Bignonia tecoma* does not appear in the Kew Index, but only *Bignonia tecomoides*, which is, however, a shrubby species.

The sugar in bilberries is entirely invert sugar (Windisch and Boehm, Zeitsch Nahr. Genussm. 1908, 8, 347). The ash contains:

K_2O	Na_2O	CaO	MgO	Fe_2O_3	Mn_3O_4	P_2O_5	SO_3	SiO_2
57·1	5·2	8·0	6·1	1·1	2·1	17·4	3·1	0·9

(Borggreve and Homberger, Bied. Zentr. 1886, 487).

Bilberries contain a red-brown dye, insoluble in acidified water and a soluble dye which, when boiled with acid, yields sugar and the insoluble colouring matter (Weigert, Bied. Zentr. 1896, 25, 58).

The juice of this berry (Ger. *Heidelbeere*) is used for colouring wines. The colouring matters of grapes and of bilberries behave in an almost identical way with most reagents (Andrée, Arch. Pharm. [3] 13, 90; Ber. 13, 582; Plahl, Chem. Zentr. 1907, i. 837).

To detect bilberry juice in wine, 50 c.c. of the wine is made faintly alkaline with sodium hydroxide, and evaporated to half its volume. After cooling it is made up to the original volume and precipitated with lead acetate. The filtrate is then precipitated with sodium sulphate and after filtration the solution is acidified with hydrochloric acid. If any vegetable colouring matter is still present, the solution at once becomes red, but the blue colour given by bilberry only appears on heating the solution in a boiling water-bath. In this way 2 p.c. of bilberry juice can be detected (Plahl, Chem. Zentr. 1908, i. 1482).

According to Vogel (Ber. 21, 1746), the colouring matter of grapes and of bilberries can be readily distinguished by their absorption spectra, providing the wine is not too concentrated, and after adding a trace of alum solution, it is carefully neutralised with ammonia. After long keeping, however, the colouring matters cannot be distinguished in this way.

The colouring matter of the juice can be extracted by neutralising it with caustic soda and then treating it with hide powder. After two days the hide powder containing the colouring matter is filtered off, washed with water, and treated with dilute hydrochloric acid, after which it is precipitated with dilute soda. The colouring substance, probably $C_{10}H_{12}O_3$, is soluble in mineral and organic acids, but insoluble in water, alcohol, ether, chloroform, or benzene. It reduces Fehling's solution, and is decomposed by hot conc. sulphuric acid, a compound $C_{14}H_{14}O_7$ being thrown down when water is added to the red solution thus obtained. The colouring matter is oxidised by nitric acid to oxalic and picric acids. It slowly decomposes on standing, evolving carbon dioxide, and its solution when treated with copper sulphate or zinc chloride, turns violet; with lead acetate it turns blue, and with ferric chloride dark-brown (Nachen, Chem. Zentr. 1895, 66, 1084).

Considerable quantities of citric and malic acids are present in the juice, which also contains hydrocarbons, glucoses, pentoses, and inositol (Nachen, *l.c.*). Ammonia turns bilberry juice a brownish-green; nitric acid in the cold blue, changing to red and becoming orange on boiling; lead acetate gives a blue precipitate, copper sulphate a violet colour, sodium carbonate a blue-black, and borax an amaranth red (Griessmayer, Chem. Zentr. 8, 381).

When chlorine is passed into the juice, a bright-grey amorphous precipitate is obtained (Nachen, *l.c.*).

(For quantitative analysis of the juice, compare Mathes, Muller, and Ramstedt (Chem. Zentr. 1905, i. 407); Lühring, Bohrisch, and Hepner (*ibid.* 1907, ii. 1755); Shamm and Jegin (*ibid.* 1907, i. 983); Behre, Grosse, and Schmidt (*ibid.* 1909, i. 456).)

When the juice is fermented, the products include aldehyde, and capric, propionic, valeric, and butyric acids (Nachen, *l.c.*).

Wine has been prepared from bilberry juice by allowing it to ferment spontaneously when mixed with a third its weight of honey. The wine thus prepared bears prolonged storage, is rich in alcohol and tannin, is of a rich clear colour, and has an agreeable flavour (Graftien, Bl. Assoc. Belge des chim. 12, [3] 107; Otto, Bied. Zentr. 1899, 28, 284).

When bilberries are extracted with chloroform, the solution evaporated, and the residue extracted with light petroleum, the soluble portion yields a wax, m.p. 71°, and a crystalline compound, probably *vitin*, m.p. 255°–260° $[\alpha]_D + 60{\cdot}72°$ (Seifert, Landw. Versuchs-Stat. 45, 29).

BILE. Bile is the secretion of the liver which is poured into the duodenum (the first part of the small intestine). It can be collected in animals by means of a biliary fistula; the same operation has occasionally been performed in human beings. After death, the gall bladder yields a good supply of bile, which is more concentrated than that obtained from a fistula. The amount of bile secreted is differently estimated by different observers; in man it probably varies from 500 to 1000 c.c. per diem.

Its constituents are the bile salts proper (sodium glycocholate and taurocholate), the bile pigments (bilirubin and biliverdin), a mucinoid substance, small quantities of fats, soap, cholesterol, lecithin, urea, and mineral salts, of which sodium chloride and the phosphates of calcium and iron are the most important.

Bile is a yellowish, reddish-brown, or green fluid, according to the relative preponderance of its two chief pigments. It has a musk-like odour, a bitter-sweet taste, and is alkaline to litmus. The specific gravity of human bile is 1·026 to 1·032 from the gall bladder, and about 1·011 when derived from a fistula. The greater concentration of gall-bladder bile is partly explained by the addition to it from the wall of that cavity of the mucinoid material it secretes. The following table will, however, show that the low percentage of solids in fistula bile is due mainly to paucity of bile salts. This is accounted for in the way first suggested by Schiff—that there is normally a bile circulation going on in the body, a large quantity of the bile salts that pass into the intestine being first split up, then re-absorbed and again synthesised and secreted. This would obviously be impossible in cases where all the bile is discharged to the exterior through a fistula. The following is the table in question, the results being the mean of several analyses of human bile:—

Constituents	Fistula bile	Gall-bladder bile
Bile salts	0·42	9·14
Cholesterol, lecithin, fat	0·07	1·18
Mucinoid material	0·17	2·98
Pigment	0·07	
Ash	0 66	0·78
Total solids	1·39	14·08
Water (by difference)	98 61	85·92

For methods of analysing human bile, *see* v. Czyhlarz, Fuchs and v. Furth, Biochem. Zeitsch. 1913, 49, 120; Analyst, 1913, 208.

The *Fel bovinum purificatum* of the pharmacopœia is made by mixing ox bile with twice its volume of rectified spirit: this is set aside for 12 hours until the sediment subsides; the clear solution is decanted and evaporated on the water-bath until it acquires a consistence suitable for forming pills. The material so obtained consists mainly of bile salts, cholesterol, fats, salts, and a certain amount of the mucinoid material. Its yellowish-green colour is due to bile pigment. It is given in doses of 5 to 10 grains, usually as pills coated with keratin to obviate its deleterious action on gastric digestion. It is given mainly in cases where the natural secretion is absent or scanty, as in jaundice. But for a full description of its medicinal uses, and also for a description of the action of drugs (cholagogues) which stimulate the liver either to secrete more bile or to cause a discharge of bile already formed, the reader is referred to any standard text-book on Pharmacology.

Plattner's crystallised bile. The bile salts are soluble in water and in alcohol, but not in ether. Their solution in alcohol is therefore precipitated by ether, and this precipitate gives, with proper precautions in technique, rosettes or balls of fine needles, or 4–6 sided prisms composed of the bile salts. This preparation is known as Plattner's crystallised bile; it is usually made from ox bile, in which case the main constituent is sodium glycocholate.

The bile salts. The sodium salts of glycocholic and taurocholic acids are those most frequently found. The former is more abundant in the bile of man and herbivora, the latter in carnivora. *Glycocholic acid* ($C_{26}H_{43}NO_6$) *is* by the action of dilute alkalis and acids, and also in the intestine, hydrolysed and split into glycine (amino-acetic acid), and cholalic (cholic) acid

$$C_{26}H_{43}NO_6+H_2O=C_2H_5NO_2+C_{24}H_{40}O_5$$

Its sodium salt has the formula $C_{26}H_{42}NaNO_6$. Taurocholic acid ($C_{26}H_{45}NO_7S$) similarly splits into taurine (amino-ethyl sulphonic acid) and cholalic acid

$$C_{26}H_{45}NO_7S+H_2O=C_2H_4\cdot NH_2\,HSO_3+C_{24}H_{40}O_5$$

Its sodium salt has the formula $C_{26}H_{44}NaNO_7S$. These substances usually are detected by Pettenkofer's reaction; small quantities of cane sugar and sulphuric acid added to the bile produce a brilliant purple colour. This is due to the interaction of furfuraldehyde (produced from the sugar and sulphuric acid) and cholalic acid.

Throughout the animal kingdom considerable variations are found in the bile salts. Thus in many fishes potassium instead of sodium salts are present. There are also variations in the bile acids themselves; for instance, in the pig hyoglycocholic acid ($C_{27}H_{43}NO_5$) takes the place of ordinary glycocholic acid, and in the goose chenotaurocholic acid ($C_{29}H_{49}NSO_6$) of ordinary taurocholic acid.

A good deal of work has been expended on the constitution of cholalic acid, but much yet remains to be done. According to Mylius, it is a monobasic alcohol acid with a secondary and two primary alcohol groups. Its formula may therefore be written $C_{20}H_{31}\left\{\begin{matrix}CHOH\\(CH_2OH)_2\\COOH\end{matrix}\right.$. On oxidation it yields other acids, which have been named dehydrocholalic acid ($C_{24}H_{34}O_5$), bilianic acid ($C_{24}H_{34}O_8$), cilianic acid ($C_{20}H_{30}O_8$): on reduction desoxycholalic acid ($C_{24}H_{40}O_4$) is obtained.

Choleic acid is another cholalic acid, with the formula $C_{24}H_{40}O_4$, found in small quantities in the bile of ox and man. It is probably identical with desoxycholalic acid. Fellic acid ($C_{23}H_{40}O_4$) is still another acid obtainable from human bile along with the ordinary acid. The principal cholalic acid in bear's bile is termed ursocholeic acid ($C_{18}H_{28}O_4$ or $C_{19}H_{30}O_4$) by Hammarsten. The same investigator finds in the walrus that the principal bile acids are *α*-phocætaurocholic acid, the cholalic acid from which has the formula $C_{22}H_{30}O_5$; and *β*-phocætaurocholic acid, the cholalic acid from which differs in certain particulars from ordinary cholalic acid, although it has the same empirical formula; he terms it *iso*cholalic acid.

The bile pigments. Bilirubin has the formula $C_{32}H_{36}N_4O_6$, and biliverdin contains more oxygen $(C_{16}H_{18}N_2O_4)n$; in bile exposed to the air, bilirubin is fairly rapidly oxidised to biliverdin. It has been proved by physiological experiment that the bile pigment is an iron-free derivative of the blood pigment; it is, in fact, identical with the substance termed hæmatoidin, which occurs usually in crystalline form in extravasations of blood in the body, as in a bruise. The bile pigment shows no absorption bands with the spectroscope, and is detected by various colour reactions, of which the most familiar is Gmelin's test; this consists in the play of colours—green, blue, red, and finally yellow—produced by the oxidising action of fuming nitric acid. The end or yellow product is called choletelin ($C_{32}H_{36}N_4O_{12}$). By reduction outside the body, a product called hydrobilirubin ($C_{32}H_{40}N_4O_7$) is obtained. A similar but not identical reduction product containing less nitrogen than hydrobilirubin is formed in the intestine, and constitutes stercobilin, the pigment of the fæces. Some of this is absorbed and ultimately leaves the body in the urine, where it is termed urobilin. A small quantity of urobilin is sometimes found preformed in the bile.

Bile mucin. The viscous material in the bile of some animals (*e.g.* man) is true mucin; in other (*e.g.* the ox) it is a nucleoprotein.

Cholesterol. Of the other constituents of the bile, cholesterol or cholesterin is the most interesting; although normally present in traces only, it may occur in excess and form the concretions known as gall stones, which are usually more or less tinged with bile pigment. It is a monatomic unsaturated alcohol, with the empirical formula $C_{27}H_{45}{\cdot}OH$. Windaus and others have shown that it is a member of the terpene series, which had hitherto only been found as excretory products of plant life.

The physiological uses of bile.—Bile is doubtless to some extent an excretion. Some state that it has a slight lipolytic action; and in some animals it certainly has a feeble diastatic power. Its main action, however, is to assist pancreatic digestion; this it does not only because its alkalinity is useful in helping to neutralise the acid mixture which leaves the stomach (chyme), but it also acts as a coadjutor to the enzymes of pancreatic juice. This is true for the proteolytic enzyme (trypsin), and the amylolytic enzyme (amylopsin), but is especially so in the case of pancreatic lipase; some go so far as to speak of the bile salts as the co-enzyme of this ferment.

In virtue of the properties which the bile salts possess of lowering surface tension, the products of fat-cleavage pass more rapidly through membranes moistened with bile than through these which are not. There is a good deal of evidence that the same holds *intra vitam*, and thus the presence of bile aids the absorption of fats by the mucous membrane which lines the intestinal wall. Bile also is a solvent of fatty acids.

When the bile meets the chyme, the turbidity of the latter is increased owing to the precipitation of unpeptonised protein. This action of the bile salts is probably useful, as it converts the chyme into a more viscid mass, and somewhat hinders its progress along the first part of the intestine, so allowing digestion and absorption to occur there.

Bile is said to be a natural antiseptic, but it is very doubtful if it is really efficient in reducing the putrefactive processes in the bowel. The bile salts are *in vitro* very feeble germicides, and the bile itself is readily putrescible; any power it may have in lessening putrescence in the intestine is due chiefly to the fact that by increasing absorption it lessens the amount of putrescible material in the intestinal tract. It is stated also that bile increases the peristaltic action of the large intestine.

Industrial and commercial uses of bile.—Apart from a somewhat limited use as a therapeutic agent, to which allusion has already been made, bile has but little commercial importance. It is, however, employed for cleansing woollen goods, and, as housekeepers know, is specially useful in cleaning carpets. This is probably connected with its power of lowering surface tension. Bile is also used by artists to ensure the uniform spreading of water colours on paper.

No attempt has been made in the foregoing article to allude to the very extensive literature of bile. This relates almost exclusively to the physiology and pathology of bile, and the important references can be best obtained from some standard work on Physiological Chemistry.

W. D. H.

BIOGEN or **MAGNESIUM PERHYDROL.** Trade name for a mixture of magnesia and magnesium peroxide.

BIOTITE *v.* Mica.

BIRCH BARK. *Betula.* (*Birke*, Ger.; *Bouleau*, Fr.) The inner bark is used in India as a substitute for paper and for lining the roofs of houses (Dymock, Pharm. J. [3] 10, 661).

It contains good tanning materials, yielding bright-yellow leather (Wagner's Jahr. 30, 1206; Trotman and Hackford, J. Soc. Chem. Ind. 1905, 1096; Bögh, Chem. Zentr. 1906, i. 1915).

The dry distillation of birch bark yields a tar and an acid aqueous solution (Kuriloff, J. Russ. Phys. Chem. Soc. 23, 98). The chief constituents of birchwood tar creosote are guaiacol and 1 : 3 : 4-creosol, together with traces of phenol, cresol, and 1 : 3 : 4-xylenol (Pfreager, Arch. Pharm. 228, 713). According to Hirschsohn (Pharm. Centr. H, 1903, 44, 845) birch tar is often adulterated with crude naphtha or naphtha residues, but the adulterated can be distinguished from the pure product by the fact that the former is only partially soluble in acetone, whereas the latter is wholly soluble.

When warm birch tar is treated with air, oxygen, or ozonised air, a pleasant-smelling solid product is obtained, soluble in alkalis, but almost insoluble in alcohol, benzene, and ether. It and its salts can be employed in medicine, pharmacy, and technically. At the same time, readily condensible liquid products distil over, which can also be used medicinally and technically, as antiseptics and in perfumery (Friedländer's Fortschr. der Teerfabr. 1905–7, 930).

A colouring substance employed in pharmaceutical and cosmetic preparations is obtained when the bark of young birch trees is soaked in water containing about $\frac{1}{20}$ of its weight of bicarbonate of soda or other carbonate. It is then boiled and filtered. Hydrochloric acid is added to the red-brown filtrate until a precipitate is formed which is filtered, washed, and dried at a gentle heat. It should be kept in well-stoppered vessels (Friedländer's Fortschr. der Teerfabr. 1897–00, 661).

The bark contains a crystalline substance termed *betulin* $C_{32}H_{60}O_3$, m.p. 257·8°, sublimes in a current of air, readily yields an anhydride at 130°, and is tasteless and odourless. It does not combine with acids or alkalis, is insoluble in water, sparingly soluble in alcohol, readily in ether and turpentine.

It is prepared by mixing the powdered epidermis of *Betula alba* with 1–8 p.c. of potassium nitrate, pressing the mixture into small tablets, and burning them in closed chambers without flame, and with the introduction of a regulated supply of air. The betulin so formed is used as films for certain substances in which it acts as an antiseptic, as a protection against damp or against corrosive acids (Wheeler, Pharm. J. 1899, 494).

The films can be deposited direct on various substances by allowing the vapours to play upon them. By a slight modification the films can be made to have a greater or less degree of transparency and porosity (Wheeler, Chem. Zentr. 1900, ii. 798).

According to Wheeler (J. Soc. Chem. Ind. 1899, 606), when birch bark or materials made from the latter, containing betulin are heated in a closed chamber and in a current of air, substances termed *pyrobetulin* and *pyrobetulin anhydride* are produced in forms other than films.

Gaultherine $C_{14}H_{18}O_8{,}H_2O$, a glucoside, is obtained by extracting the bark of *Betula lenta* with alcoholic lead acetate, precipitating by ether, and recrystallising from alcohol. The aqueous solution has a bitter flavour, is lævo-rotatory, and reduces Fehling's solution when boiled. It is hydrolysed by mineral acids, baryta, and by water when heated to 130°–140°, giving a sugar and methyl salicylate (Schaugans and Geroch, Arch. Pharm. 232, 437).

A gum of probable formula $C_4H_4O_3$ has been isolated from American birch wood (*Betula alba*) (Johnson, Amer. Chem. J. 1896, 214).

Birchbark oil is obtained by distilling birch bark (*Betula alba*) in steam. It is brown, and has a similar odour to birch bud oil. On cooling, crystals separate. It contains palmitic acid (Haensel, Chem. Zentr. 1907, ii. 1620; Ziegelmann, Pharm. Review, 1905, 23, 83).

The birch bark oil prepared from the bark of *Betula alba* by Haensel (Chem. Zentr. 1908, ii. 1436), had sp.gr. 0·9003 at 20° and $[\alpha]_D -12{\cdot}08°$; a colourless monocyclic sesquiterpene was isolated from it, having b.p. 255°–256°/744 mm., sp.gr. 0·8844 at 20°, and $[\alpha]_D -0{\cdot}5°$. The terpene yields a hydrochloride, sp.gr. 0·9753 at 20°, and a hydrocarbon, b.p. 258°–260°/747 mm., and sp.gr. 0·8898 at 20°.

Birch oil, or the wintergreen oil of commerce, is obtained from the twigs of North American birches, especially the *Betula lenta*, but the pure genuine oil is prepared from *Gaultheria procumbens* (J. Soc. Chem. Ind. Abstr. 1893, 174). It consists of methylsalicylate, a hydrocarbon $C_{15}H_{24}$, and small quantities of benzoic acid and ethyl alcohol (Schroeter, Amer. J. Pharm. Aug. 1889; Trimble and Schroeter, Pharm. J. 20, 166; Ziegelmann, *l.c.*).

Oil of *Gaultheria procumbens* contains 99 p.c. methylsalicylate, together with some paraffin —$C_{30}H_{62}$—probably triacontane; an aldehyde or ketone; a secondary alcohol $C_8H_{16}O$, and an ester $C_{14}H_{24}O_2$, and is lævo-rotatory, sp.gr. 1·180; that obtained from the birch contains 99·8 p.c. methylsalicylate, together with the above constituents except the alcohol $C_8H_{16}O$, which is absent. It is optically inactive; sp.gr. 1·187 (Pharm. J. 1895, 307, 328).

Birch bud oil is obtained by the distillation of birch buds with steam. It is yellow, and has a pleasant aromatic odour. Crystals separate out at ordinary temperatures, and it becomes wholly crystalline at −45° (J. Soc. Chem. Ind. 1903, 228). It is soluble in alcohol and in ether, but not in alkalis, carbon disulphide, or glacial acetic acid. It is lævo-rotatory, its rotation and specific gravity varying with different preparations. That obtained by Schimmel (Chem. Zentr. 1909, ii. 2156) had sp.gr. 0·9730 at 15° and $\alpha_D -5°\ 34'$.

It contains a paraffin, m.p. 50°, an ester, and a sesquiterpene alcohol, *betulol*, probably $C_{15}H_{23}OH$, which is very much like amyrol (obtained from sandalwood oil), has a bitter taste, an odour like incense, b.p. 284°–288°/743 mm., 138°–140°/4 mm.; sp.gr. 0·975; $[\alpha]_D -35°$ (von Soden and Elze, Ber. 38, 1636; Haensel, Chem. Zentr. 1909, ii. 1156. Compare also Pharm. Zeit. 47, 818; Schimmel, Chem. Zentr. 1905, i. 1340).

The leaves of *Betula alba* yield an olive-green oil, which is solid at ordinary temperature, but fluid at 35°, has sp.gr. 0·9074 at 35°, and is optically inactive (Haensel, Chem. Zentr. 1904, ii. 1737).

Haensel (Chem. Zentr. 1908, i. 1837) has isolated a crystalline paraffin, m.p. 49·5°–50°, from the oil of birch leaves.

According to Grasser and Purkert (Chem. Zentr. 1910, i. 489), products $C_{41}H_{70}O_7$, $C_{39}H_{68}O_8$, readily soluble in water, and of which the potassium salt $C_{41}H_{67}K_3O_7$ can be used therapeutically as a diuretic, can be obtained by extracting birch leaves with alcohol, treating the warm extract with potassium hydroxide, and then saturating the solution with dry carbon dioxide. Water is now added and the insoluble products filtered off. The filtrate is concentrated, the soluble products precipitated with a mineral acid, and separated from one another by conversion into their di- and trialkali derivatives.

Birch juice obtained from birch trees contains lævulose, a large quantity of malates, and basic constituents. When fermented with dextrose and milk of almonds, it forms 'birch wine' (Lenz, Ber. Deut. Pharm. Ges. 19, 332).

BIRD-LIME. (*Glu*, Fr.; *Vogelleim*, Ger.) Bird-lime, from *Ilex aquifolium* (Linn.), was found by Personne to consist, in addition to vegetable *débris* and water, of calcium oxalate, caoutchouc, and ethereal salts of a solid crystalline substance, *ilicic alcohol* $C_{25}H_{44}O$, m.p. 175°, with undetermined fatty acids.

According to Divers and Kawakita, Japanese bird-lime, made from *I. integra*, contains ethereal salts of palmitic acid, and in very small quantity a semi-solid acid, the calcium salt of which is soluble in ether and in alcohol. Japanese bird-lime also yields two very similar alcohols by hydrolysis, one differing only slightly from ilicic alcohol, and termed *ilicylic alcohol* $C_{22}H_{38}O$, m.p. 172°, and another named *mochylic alcohol* $C_{26}H_{46}O$, m.p. 231°, from *mochi*, the Japanese word for bird-lime.

Caoutchouc is also present in Japanese bird-lime to the extent of about 6 p.c., but only minute quantities of oxalates. By distillation, bird-lime yields much palmitic acid and a thick oily hydrocarbon $C_{26}H_{44}$ (Divers and Kawakita, Chem. Soc. Trans. 1888, 268).

BIREEZ. Persian name for gum galbanum (Dymock, Pharm. J. [3] 9, 1016).

BISABOL *v.* Myrrh, art GUM RESINS.

BISCINIOD. Trade name for a combination of cinchonidine hydriodide and bismuth iodide.

BISDIAZONIUM SALTS *v.* DIAZO COMPOUNDS.

BISMAL. Bismuth methylene digallate (*v.* BISMUTH, Organic compounds of; also SYNTHETIC DRUGS).

BISMARCK BROWN *v.* AZO- COLOURING MATTERS.

BISMITE or **BISMUTH-OCHRE.** Native bismuth oxide, Bi_2O_3, occurring as a yellow earthy powder, or as minute rhombohedral scales. Analysis of various bismuth-ochres from the tourmaline mines of San Diego Co., California, show these to be either bismuth hydroxide, $Bi(OH)_3$, or pucherite, $BiVO_4$, or mixtures of these; and doubt has been expressed as to the occurrence of the pure oxide Bi_2O_3 in nature (W. T. Schaller, 1911). L. J. S.

BISMON *v.* SYNTHETIC DRUGS.

BISMUTH. *Bismuth.* (*Etain de glace*, Fr.; *Wismuth*, Ger.) Symbol Bi. At. wt. 208·5 (De Coninck and Gérard).

Occurrence.—Metallic bismuth occurs in small quantities in widely distributed localities, usually with other ores, such as those of cobalt, nickel, copper, silver, lead, and tin. It is found massive, granulated, reticulated or arborescent, associated with arsenic and silver, and occasionally iron.

The principal sources are Bolivia, South Australia, Altenberg, Schneeberg, Annaberg, Marienberg, Joachimsthal, Johanngeorgenstadt, Lölling in Carinthia, Fahlun, Sweden, and New South Wales. In small quantities it occurs at Huel Sparnon, Cornwall, Carrick Fells, Alva, Stirlingshire. Alloyed with 64 p.c. gold it occurs at Maldon, Victoria. Alloyed with tellurium it occurs as *tetradymite* in Cumberland. An alloy of bismuth with 3 p.c. arsenic occurs at Palmbaum near Marienberg.

Bismuth sulphide is widely distributed in small quantities, being found in Saxony, Sweden, South Australia, America, and Cumberland. A sulphide of bismuth, copper, and lead occurs as *needle ore*, *aciculite* or *patrinite*.

As oxide, or *bismuth ochre*, it is found as a yellow substance, frequently as a coating on other minerals, associated with iron and other impurities, at Schneeberg, Joachimsthal, Beresof in Siberia, and in New South Wales. The principal ore in Bolivia, which is stated by Domeyko to be the richest country in bismuth, is a compact earthy hydrated oxide.

Bismuth occurs as carbonate or *bismuthite*, usually containing carbonates of iron and copper, at Meymac, with antimony, arsenic, lead, iron, and lime; in Mexico, whence it is imported to this country; in North Carolina, and other localities. Of late years considerable deposits of bismuth ores have been found in many places in America, but they have been very little worked.

Extraction.—At Schneeberg in Saxony the ore worked is principally metallic bismuth occurring in ores which contain silver, lead, tin, and arsenic in gneiss and clay-slate.

The ore, which contains from 7 to 12 p.c. bismuth, is sorted by hand as far as possible from the gangue before treatment. The old method of *liquation* or 'sweating' is still used, but has now been largely superseded by smelting processes, in which the metal is much more perfectly extracted.

Liquation.—In this process the metal is separated as far as possible from the gangue by melting at a low temperature. The picked ore is broken into pieces as large as a hazel nut, and placed in inclined iron tubes in charges of about 12 cwts., sufficient space being left in the tube for stirring the ore from the upper end (Figs. 1, 2, 3). The tubes are closed at the upper ends by plates of iron, and at the lower ends by similar plates containing circular apertures through which the molten metal may run. The ends of the tubes project slightly beyond the walls of the furnace, the upper over a tank and the lower ends over iron crucibles which contain powdered charcoal, and which are gently heated from below by a small charcoal furnace. The tubes are heated so as to cause the metal to flow easily, and in about 10 minutes the bismuth commences to pass out into the crucibles, being there covered by the charcoal and thus protected from oxidation. The ore is occasionally stirred with an iron rod from the upper end, and in from 30 to 60 minutes the operation is completed. The residues, *graupen* or *bismuth barley*, are raked from the upper end into the tank, and at once replaced by fresh ore. In this manner only about two-thirds of the bismuth is extracted. 20 cwts. of ore require 63 cubic feet of wood. The contents of the pots are removed by ladles to moulds and cast into ingots of 25 to 50 lbs. weight.

Sulphurous ores are usually roasted to remove sulphur, and then smelted with iron (to remove the last traces of sulphur), carbon, slag, sodium carbonate, limestone, and sometimes fluor-spar. The regulus of bismuth thus obtained is fused on an inclined iron plate and run down, leaving a dross containing much of the impurity. Bismuth ores are sent from Joachimsthal, and worked by this process at Schneeberg.

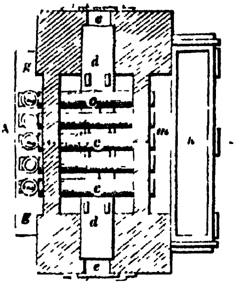


Fig. 1.

The following analyses of two typical samples show the composition of commercial bismuth: From Saxony—Bismuth, 99·77 p.c.; copper, 0·08; silver, 0·05; sulphur, 0·10; iron, trace From Joachimsthal—Bismuth, 99·32 p.c.; lead, 0·30; silver, 0·38; iron and copper, traces; sulphur, none

At Joachimsthal a method devised by R Vogel is used (Dingl. poly. J. 167, 187) for extracting bismuth from ores free from lead. The ores, which usually contain from 10 to 30 p.c. bismuth, are mixed, according to their richness, with 23 to 30 p.c. iron turnings, 15 to 50 p.c. sodium carbonate (according to the amount of gangue present), 5 p.c. lime, and 5 p.c. fluor-spar. The mixture is introduced in charges of about 1 cwt. into clay crucibles, 23 inches high and 16 inches wide at the mouth, covered and heated in a wind furnace to tranquil fusion, and poured into conical moulds. The liquid separates into three layers, the upper consisting of slag, the second of a speiss containing the arsenic, sulphur, nickel, cobalt, and iron, and most of the other impurities, with about 2 p.c. of bismuth, and the lower consisting of a regulus of nearly pure bismuth. The metal is again fused and remoulded (*see* Kerl, Handb. der Met. Hüttenkunde).

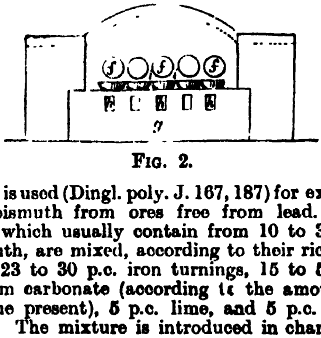


Fig. 2.

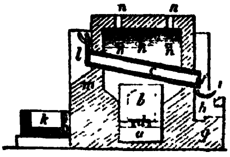


Fig. 3.

A similar process has been adopted by Patera (J. 1862, 646) for the extraction of bismuth from refinery residues.

In France the carbonate of bismuth imported from Meymac is dissolved in the minimum quantity of hydrochloric acid and pieces of iron inserted in the slightly acid liquid. The bismuth is thus precipitated as a black powder, which is well washed and fused in a plumbago crucible under a layer of charcoal at as low a temperature as possible (Ad. Carnot, Ann. Chem. Phys. [5] 1, 405; and Bull. Soc. chim. 21, 114).

Ores of bismuth averaging 60 p.c. bismuth are imported into England, principally from Adelaide, South Australia, and from Mexico. They are usually fused in plumbago pots with borax, sodium carbonate, and a little crude tartar.

For the extraction of bismuth for pharmaceutical purposes from sulphurous ores, Valenciennes roasts the ore on the level bed of a reverberatory furnace for 24 hours with the occasional addition of charcoal and frequent stirring with an iron rabble. When the sulphur has thus been evolved, the ore is mixed with about 30 p.c. charcoal, and a mixture of chalk, salt, and fluor-spar, and again fused in a reverberatory furnace. From 5 to 8 p.c. of the bismuth is lost by this process, but this is compensated by the extra purity of the product. By subsequent fusion with nitre, the antimony, arsenic, and sulphur are removed, and by the ordinary wet methods the lead, copper, and silver are eliminated (M. A. Valenciennes, Ann. Chim. Phys. [5] 1, 397).

H. Tamm (Chem. News, 25, 85) states that bismuth can be separated from ores containing much copper by fusion with an alkaline flux containing free sulphur, in which case the copper remains unreduced. He recommends a mixture of 5 parts sodium carbonate, 2 salt, 1 sulphur, 1 carbon, to be mixed in about equal proportions with the ore. The bismuth produced is stated to be much more free than usual from arsenic, antimony, and lead, but about 8 p.c. of the total bismuth is lost.

The bismuth present in small quantities in lead, copper, and silver ores frequently becomes concentrated in the secondary products of the metallurgical processes and may then be profitably extracted. In the oxidation of silver-lead containing bismuth, the lead oxidises much more rapidly than the bismuth, and at the close of the cupellation a blackish litharge rich in bismuth is obtained, from which that metal may be extracted by further concentration and acid treatment (J. 12, 711). In this manner bismuth becomes concentrated in the *blicksilber* in the treatment of silver ores at Freiberg, and passes into the hearth bottoms, as much as 25 p.c. being sometimes so absorbed. When the hearths contain sufficient bismuth to be profitably extracted, they are finely ground and treated with hydrochloric acid, with the formation of bismuth chloride. Water is added to the solution to precipitate the metal as oxychloride, and the precipitate is collected, washed, dried, and reduced to metal by fusion with charcoal, sodium carbonate, and powdered glass (*v.* Phillips's Metallurgy).

Several proposals have been made for the extraction of bismuth by wet methods. Becker (Fr. Pat. 366439, 1906) suggests the treatment of sulphide ores with a solution of an alkali or alkaline earth hyposulphite. The solution thus obtained is treated with alkali sulphides, and the resulting precipitate of bismuth sulphide is dried and smelted as described above.

Both Becker (*ibid.*) and Ranald (Eng. Pat. 16622, 1898) have patented the use of a solution of ferric chloride as a solvent for bismuth sulphide and the subsequent precipitation of metallic bismuth from the solution by means of iron or zinc, or by electrolysis.

Eulert (Rev. Prod. Chim. 4, 164) employs a mixture of sulphuric acid, water, common salt, and potassium nitrate as the extracting liquor, and the process can be made continuous. The bismuth is finally obtained as the oxychloride, which can be sold or smelted for the metal.

On the extraction of bismuth from its ores, *v.* also Winckler (Ber. Entwick. Chem. Ind. 1, 953).

Purification.—The crude bismuth produced by the above methods contains a variety of impurities, from which it is important in many cases to separate it. These impurities are sulphur, arsenic, antimony, copper, nickel, cobalt, silver, gold, lead, and iron.

Sulphur and arsenic may be removed by fusion with $\frac{1}{10}$ of its weight of potassium nitrate, with constant stirring at a temperature slightly above the temperature of fusion; the nitre soon oxidises the impurities and a little of the bismuth, forming with them a slag which rises and solidifies at the surface. For the complete removal of these impurities a second fusion is frequently necessary.

C. Méhu (Pharm. J. [3] 4, 341) recommends the following process for the removal of sulphur and arsenic. The metal is heated considerably above the melting-point in a vessel so as to expose a large surface, and the oxide is removed to the sides as fast as it forms until about one-fourth of the metal has become oxidised; the greater part of the sulphur and arsenic will then have passed off as oxides. The mass is cooled, pulverised, and mixed with charcoal, dried soap, and potassium carbonate (free from sulphate), about one-fourth of the original weight of the metal, in a crucible, covered with charcoal, and heated to redness for one hour. Arsenic may also be mostly removed by fusion for a considerable time under a layer of charcoal. Arsenic, sulphur, and most of the antimony may be eliminated by fusion at a bright-red heat under borax, stirring with a rod of iron until the action ceases. The iron combines with the impurities and rises as a difficultly fusible slag to the surface from beneath which the still liquid metal may be poured after partial cooling.

For the complete removal of *antimony*, 2 or 3 parts of bismuth oxide for each part of antimony supposed present are fused with the metal. The oxide of bismuth then gives up its oxygen to the antimony, becoming itself reduced and the antimonious oxide floats on the surface.

Hugo Tamm (Chem. News, 25, 85) recommends for the removal of *copper* the fusion of the metal at a low temperature under 1 part of a mixture of 8 potassium cyanide and 3 sulphur. When the action has ceased the mass is stirred with a clay (not iron) rod, cooled until the flux has set, and the metal poured out from beneath. If impure cyanide is used, a relatively larger quantity is required.

Iron may be completely removed, according to H. Türach (J. pr Chem. [2] 14, 309), by fusion under a layer of potassium chlorate containing from 2 to 5 p.c. sodium carbonate.

From *silver* bismuth may be separated by cupellation and subsequent reduction of the bismuth oxide so produced, or the metal may be dissolved in nitric acid, the silver precipitated with hydrochloric acid, the solution filtered, and the basic salt of bismuth precipitated by excess of water, and reduced to metal.

Silver can be partially removed from bismuth by a process resembling Pattinson's process for lead (Schneider, J. pr. Chem. [2] 23, 75).

Lead may be precipitated from a nitric acid solution of the metal by the addition of sulphuric acid, and the bismuth recovered as already described. A method commonly used is to fuse the impure metal with bismuth oxychloride, from which the lead liberates bismuth, itself becoming combined with oxygen and chlorine.

A number of investigations on the refining of bismuth have been conducted by E. Matthey, and the methods he proposes are given separately below, inasmuch as they possess the merit of simplicity and have been thoroughly tested on a large scale.

Arsenic is removed completely by maintaining molten bismuth at a temperature of 510°–520° for some time. There is only a very slight loss due to oxidation (E. Matthey, Chem. News, 67, 63).

Antimony is separated by melting the metal and maintaining the temperature at 350°. An alloy of bismuth and antimony, containing over 30 p.c. of the latter, rises to the surface of the metal, giving it an 'oily' appearance, and can be skimmed off. A complete removal of the antimony is thus effected (E. Matthey, *l.c.*).

Copper. For the separation of copper from bismuth which has been previously freed from arsenic, antimony, lead, &c., E. Matthey (Roy. Soc. Proc. 43, 172) recommends its fusion with bismuth sulphide. The pure metal obtained amounts to 90 p.c. of the crude material, while the remaining bismuth sulphide, containing copper sulphide, may be resmelted.

Alkali sulphides may be substituted for the bismuth sulphide in the above operation (E. Matthey, Proc. Roy. Soc. 49, 78).

Lead may be separated from the fused metal by repeated crystallisations, the alloy of bismuth and lead melting at lower temperatures than the purer bismuth. E. Matthey has thus by four crystallisations reduced the percentage of lead from 12 to 0·4 p.c. (Proc. Roy. Soc. 42, 93).

For the separation of *gold* and *silver*, E. Matthey (Proc. Roy. Soc. 42, 89, 94) recommends the addition of 2 p.c. zinc to the molten metal. The mass is gradually cooled and the surface crust removed. This operation is repeated, whereby the whole of the precious metals are concentrated in the skimmings. On fusing these in a crucible with borax, the gold and silver are freed from impurities by the action of the oxide of bismuth, and sink to the bottom. To separate the last traces of these metals from the slag, it is again fused with bismuth.

A. Mohr states (Elektrochem. u. Met. Ind. 1907, 5, 314) that an electrolytic method has been used with success for the purification of a Mexican lead-bismuth alloy containing 81·1 p.c. lead and 14·5 p.c. bismuth, together with small amounts of antimony, iron, zinc, arsenic, silver, and gold. First the metal is made the anode in an electrolyte containing 6 p.c. lead fluosilicate and 14 p.c. hydrofluosilicic acid. The lead is deposited on a cathode of pure lead, and contains only 0·01 p.c. bismuth. The anode slimes are fused with sodium hydroxide and carbonate, and the metal, containing 94 p.c. bismuth, cast into anodes, which are then used in a second electrolysis, using a solution of bismuth chloride (about 10 p.c.) and free hydrochloric acid (about 10 p.c.). The cathodes are of Acheson graphite, and are placed on the floor of the cell. The current used is 20 amp. per sq. ft. at the cathode, and 60 amp. per sq. ft. at the anode, with a P. D. at the terminals of 1·2 volts. The resulting bismuth is 99·8 p.c. pure, the remaining 0·2 p.c. consisting chiefly of silver. (*See* also Zahorski, Hurter and Brock, Eng. Pat. 22251, 1895.)

Chemically pure bismuth is best prepared by dissolving the commercial metal in nitric acid, decanting from any residue, and adding excess of water, whereby the bismuth is precipitated as basic nitrate, leaving the impurities in solution. The precipitate is well washed by decantation, dried, mixed with black flux or other reducing agent which produces a readily fusible flux, and reduced at a gentle heat in a crucible.

Properties.—Bismuth is a greyish-white crystalline metal of distinctly red tinge when compared with whiter metals such as zinc or antimony. It is very brittle and easily powdered, and a bad conductor of heat and electricity. Its tenacity is very small, a rod 2 mm. in diameter will just support a weight of 14·19 kilos. (Muschenbroeck). It forms fine obtuse rhombohedral crystals, which approach very closely to the form of cubes. It has also been obtained in the form of acicular needles, which are really elongated hexagonal prisms (Heberdey, Ber. Akad. Wien. 104, i. 254). Bismuth melts at 271° (Mylius and Groschuff), and boils at a temperature between the melting-point of copper and nickel, *i.e.* between 1084° and 1450° (Carnelley and Carlton Williams), condensing in laminæ. The vapour density at temperatures between 1600° and 1700° is 11, which corresponds to that calculated for a mixture of monatomic and diatomic molecules (Meyer, Ber. 1889, 22, 726). Its sp.gr. at 12° is 9·823. W. Spring has shown that by the exposure of bismuth of density 9·804 to a pressure of 20,000 atmospheres, the density was raised to 9·856: a second compression still further increased the density to 9·863 (Ber. 16, 2724). It is stated that by careful hammering its density may be raised to 9·88.

Bismuth expands in cooling. Tribe (Chem. Soc. Trans.) has shown that this expansion does not take place until after solidification.

According to Cohen and Moesveld, bismuth exists in two enantiotropic modifications, the transition temperature being 75°/760 mm. The transformation of the form stable below this temperature (α) into the other modification (β) is accompanied by considerable increase in volume. The β-variety can exist in the metastable condition below the transition point.

Exposed to dry air, bismuth remains unaltered at the ordinary temperature, but in moist air or in contact with water it becomes coated with oxide. When heated in air it burns with a bluish flame, evolving yellowish fumes of oxide. At high temperatures it decomposes water.

Cold sulphuric acid has no action, but the hot concentrated acid dissolves bismuth. Hydrochloric acid acts but slowly, and Ditte and Metzner have shown (Compt. rend. 115, 1303) that this action can only take place in presence of oxygen. Nitric acid, dilute or strong, dissolves it readily, with the formation of nitrate. Powdered bismuth thrown into chlorine gas ignites with the formation of trichloride. It also unites directly with bromine, iodine, and sulphur.

When comparatively pure, bismuth crystallises readily. To obtain it in the form of fine crystals it is melted and allowed to cool until a crust has formed; the crust is pierced on opposite sides with a hot iron, and the still liquid portion poured through one of the openings. On careful removal of the crust the sides of the vessel are found covered with crystals, frequently resembling hollow pyramidal cubes like those of salt, but which are in reality obtuse rhombohedra. Their iridescent lustre is due to a very thin film of oxide which shows the colour characteristic of thin plates.

Bismuth can be obtained in the colloidal state by reducing a solution of the nitrate with stannous chloride, or by the action of hypophosphorus acid on bismuth oxychloride (Gutbier and Hofmeyer, Zeitsch. anorg. Chem. 44, 225).

Bismuth is the most diamagnetic substance known, a bar of the metal placing itself equatorially between the poles of a magnet, *i.e.* at right angles to the position taken up by a bar of iron. Bismuth also occupies an extreme place in the thermo-electric series, being used with antimony in the preparation of the most delicate thermopiles.

Analysis.—All compounds of bismuth, when mixed with carbon or other reducing agent and fused before the blowpipe, give a *brittle* white bead of metal and a yellow incrustation on the charcoal, darker than that of oxide of lead.

A very good dry test for bismuth is that due to von Kobell. The substance is heated on charcoal with a mixture of potassium iodide and sulphur, when, if bismuth is present, a brilliant scarlet incrustation is obtained.

Salts of bismuth in solution give, on addition of excess of water, a white precipitate of basic salt, which is insoluble in tartaric acid, and blackens with sulphuretted hydrogen (distinction from antimony).

Metallic iron, copper, lead, and tin precipitate metallic bismuth from solutions.

A qualitative test for bismuth proposed by Reichard (Chem. Zeit. 28, 1024) is the addition of a brucine salt, or, better, brucine itself to the solution. In presence of bismuth a deep-red colour is produced which is distinguished from that given by nitric acid by the fact that it becomes deeper on heating, whereas the colour given by nitric acid turns to yellow.

Estimation.—Bismuth may be separated from copper, cadmium, mercury, and silver, lead having been removed previously by precipitation as sulphate, by the following method, due to Stähler and Scharfenberg (Ber. 38, 3862).

The solution, which may contain hydrochloric acid, and should contain about 0·1–0·2 gram of bismuth, is diluted to 300–400 c.c., and any precipitate redissolved by the cautious addition of nitric acid. This solution is heated to boiling, and treated with a boiling 10 p.c. solution of trisodium phosphate Na_3PO_4 (obtained by mixing equivalent amounts of sodium hydrogen phosphate and caustic soda). In presence of much hydrochloric acid, a considerable excess of the phosphate must be used, but, should the solution become alkaline, nitric acid must be added. After boiling the whole for some time, the precipitate is allowed to settle, and the supernatant liquid is tested with sodium phosphate. If precipitation is complete, the precipitate is collected hot on a Gooch crucible, washed with 1 p.c. nitric acid, containing ammonium nitrate, dried at 120°, and finally heated over a bunsen burner, and weighed as bismuth phosphate $BiPO_4$. The precipitate is very hygroscopic: suitable precautions must therefore be taken in weighing it.

A modification of this method, which renders it suitable for the separation of bismuth from considerable amounts of mercury, has been described by Stähler (Chem. Zeit. 31, 615).

A volumetric method for the estimation of bismuth, for which considerable accuracy is claimed, is the chromate method of Löwe as modified by Rupp and Schaumann (J. Soc. Chem. Ind. 1902, 1558).

H. W. Rowell has published a method (J. Soc. Chem. Ind. 1908, 102) for the estimation of small quantities of bismuth in ores, &c. The method is colorimetric, depending on the yellow colour produced when potassium iodide is added to a solution of the bismuth compound in sulphuric acid (*see* also Eng. and Mining Jour. 1901, 459).

An account of other methods used for the estimation of bismuth will be found in the article on ANALYSIS.

For the dry assay of bismuth ores the fluxes used must depend on the composition of the ore. Thus with ores containing metallic bismuth or that metal as oxide, sulphide, carbonate, &c., a flux consisting of a mixture of 2 parts potassium or sodium carbonate, 1 part sodium chloride, and a proper quantity of argol or potassium cyanide or charcoal powder, will be useful (Tamm); with the addition, where much earthy matter is present, of borax. Where much *copper* is present, Tamm advises the use of one part of the ore mixed with one part or less of a mixture of sodium carbonate 1, salt 2, sulphur 2, charcoal powder 1 part. The exact proportions in which these fluxes are most useful must be learned by experience.

Alloys of Bismuth.

Bismuth unites readily with most metals, forming alloys which, with few exceptions, are not of commercial importance.

Tin and Lead. The alloys of bismuth with these two metals are of special interest. They are extremely fusible, and on account of their expansion on cooling they take a very fine impression, being largely used for electrotype moulds, &c.

An alloy of 1 bismuth, 2 tin, 1 lead is used as a soft solder by pewterers, and for the cake moulds for toilet soap. An expensive but effective alloy for stereotype clichés and metallic writing pencils contains 5 bismuth, 2 tin, 3 lead; it melts at 91·66°.

A thorough physico-chemical investigation of these ternary alloys has been made by Charpy (Compt. rend. 126, 1569), whose memoir should be consulted for details. He finds that the eutectic mixture contains 32 p.c. lead, 16 p.c. tin, and 52 p.c. bismuth, and has m.p. 96°. Such alloys are used to a considerable extent in safety plugs for boilers and for automatic sprinklers.

The varieties of *fusible metal* contain these three metals, with the addition sometimes of cadmium, which still further lowers the melting-point. A table of the most important of these alloys is given below:

Name of alloy	Bismuth	Lead	Tin	Cadmium	Melting-point	Temperature of maximum density
Newton's . .	50	31·25	18·75	—	94·5°	—
Rose's . . .	50	28·10	24·1	—	95°	55° (Spring)
D'Arcet's . .	50	25·0	25·0	—	94°	—
Lichtenberg's . .	50	30·0	20·0	—	—	—
Wood's . .	50	25·0	12·5	12·5	65°	25° (Spring)
Lipowitz's . .	50	26·9	12·78	10·4	65°	38·5° („)
Guthrie's 'Eutectic'	50	20·55	21·10	14·03	—	—

The action of heat on fusible metal is somewhat anomalous. Taking Lipowitz's alloy as a typical example, we find (from Spring's table of densities at different temperatures) that this alloy whilst cooling contracts very rapidly at the solidifying point (65°), contracts slowly from that temperature to 38·5°, expands thence to about 25°, and again contracts, occupying at 0° the same volume as at 46°.

For this reason, in taking a cast or impression with fusible metal, it is advisable to allow the alloy to cool to a pasty mass before placing in the mould (*v.* further, Godefroy, Fremy's Encycl. Chimique, art. 'Bismuth,' 1888, 24–30).

Mercury dissolves a considerable amount of bismuth without solidifying. The amalgam containing 1 bismuth and 4 mercury adheres strongly to smooth surfaces such as glass. One part bismuth and 2 parts mercury forms a pasty amalgam. The alloy consisting of D'Arcet's alloy and mercury, for which 250 parts of mercury are used for 100 parts of D'Arcet's alloy, is used, on account of its low melting-point, for taking casts of anatomical preparations. The alloy is introduced in the liquid state, allowed to solidify, and the fleshy parts dissolved by solution of caustic soda. This alloy is also used for silvering glass tubes, &c.

Bismuth alloys with the *alkali metals*; Johannis (Compt. rend. 114, 585) has obtained an alloy of bismuth and sodium, of the formula $BiNa_3$, by the action of a solution of sodium in liquid ammonia on bismuth. The compound forms small, dark-grey crystalline laminæ, m.p. 775°, and takes fire in the air. It may easily be prepared by slowly adding bismuth to sodium melted beneath paraffin heated to 300°–310° when the crystals separate out. An alloy with potassium, K_3Bi, may be prepared in a similar manner (Vournasos, Ber. 1911, 44, 3266). The alkali bismuthides are readily oxidised in the air, turning black, and burn easily, giving a red residue of alkali bismuthate. They absorb hydrogen at 350°, forming a product which is decomposed by water, evolving hydrogen. They decompose water slowly at the ordinary temperature, and more rapidly on boiling, and reduce copper salts in solution to metallic copper.

A. H. Gallatin (Phil. Mag. [4] 38, 57) has prepared an alloy of bismuth with *ammonium* (?). He scattered ammonium chloride over bismuth sodium alloy, and added water. The alloy swelled and then contracted. On plunging in water or heating, a mixture of hydrogen and ammonia was evolved. After drying *in vacuô* over sulphuric acid, it evolved 27 volumes of gas on heating.

COMPOUNDS OF BISMUTH.

Bismuth forms two well-defined classes of compounds, in which it is a diad and a triad respectively. There are indications of the existence of some more highly oxidised compounds, but, assuming their existence to be proved, their constitution can be more easily explained by the assumption of a higher valency for oxygen than by assuming bismuth to be a pentad.

Hydride. A gaseous hydride of bismuth appears to be formed by the solution of an alloy of bismuth and magnesium with thorium-C or radium-C in 0·2 N hydrochloric acid. It is fairly stable at ordinary temperatures, but is decomposed at a red heat and forms a mirror in the Marsh apparatus similar to antimony (Paneth, Ber. 1918, 51, 1704; Paneth and Winternitz, *idem.* 51, 1728).

Oxides. Only two oxides of bismuth, the dioxide and the trioxide, are definitely known. The statements of Deichler, Hauser, and Vanino and Treubert, that bismuthic acid and tetroxide exist, have been controverted by Gutbier and Bunz (Zeitsch. anorg. Chem. 48, 162; 49, 432; 50, 210; 52, 124); Moser (Zeitsch. anorg. Chem. 50, 33) states that the addition of hydrogen peroxide to a bismuth salt precipitates only bismuth trioxide. According to Hollard (Compt. rend. 136, 229) a peroxide of the formula Bi_2O_7 is formed during the electrolysis of a solution of bismuth sulphate, but this observation has not been confirmed. It is doubtful whether a suboxide exists.

The trioxide and the compounds derived from it are the only ones of commercial importance.

Bismuth trioxide Bi_2O_3 occurs in nature as *bismuth ochre*. It is best prepared by heating the subnitrate of bismuth until red fumes cease to be evolved. It may also be prepared by exposing the metal to a red-white heat in a muffle. The metal then burns and forms the oxide, which condenses as a yellow powder. Bismuth oxide thus obtained is a pale-yellow amorphous substance, which melts at a red heat to a glass without change of weight. Its sp.gr. is 8·21. Heated in sulphur dioxide it is ultimately converted into a basic sulphate $4Bi_2O_3,3SO_3$.

The oxide can be obtained crystalline, and has been shown to be isodimorphous with antimony trioxide (Muir and Hutchinson, Chem. Soc. Trans. 1889, 143).

It is used for glass and porcelain staining; as an addition to certain fluxes to prevent the production of colour; and in gilding porcelain, being mixed in the proportion of 1 part oxide to 15 parts of the gold.

The darkening of the commercial substance on exposure to light is due to the presence of a trace of silver.

A **hydrated bismuth oxide** Bi_2O_3,H_2O is precipitated as a white powder on addition of caustic alkali to a bismuthous salt, such as the nitrate; but Thibault (J. Pharm. Chim. 12, 559) has shown that under these conditions the product contains appreciable quantities of oxy- acid salts. By precipitating the hydroxide from an alkaline solution by the addition of acid, a pure product is obtained which on drying yields the pure oxide. It dissolves in alkali in presence of glycerol. On addition of sugar to the solution, metallic bismuth is precipitated, whilst arsenic, if present, remains in solution. Lowe (Zeitsch. anal. Chem. 22, 498–505) recommends this method for the preparation of pure bismuth for pharmaceutical purposes.

Bismuth carbonate $CO(O{\cdot}BiO)_2$ is best prepared by triturating powdered bismuth nitrate with mannitol under water until solution is obtained, when a strong solution of potassium carbonate is added. Bismuth carbonate separates as a fine heavy powder which is washed with water, alcohol and ether, and dried in the air (Vaning, Pharm. Zentr-h. 1911, 52, 761).

Bismuth nitrate $Bi(NO_3)_3,5H_2O$ is prepared by dissolving bismuth or its oxide or carbonate in moderately strong nitric acid. The concentrated solution is filtered, if necessary, through asbestos, and deposits on cooling large deliquescent crystals, which are caustic and melt in their water of crystallisation when gently heated.

When the bismuth used for the preparation contains arsenic, excess of nitric acid should be used for the solution; the arsenic is then oxidised to arsenic acid, and combines with its equivalent of bismuth, being precipitated as arsenate of bismuth. R. Schneider (J. pr. Chem. 20, 418–434) recommends the following proportions: 2 kilos. bismuth, 10 kilos. *hot* nitric acid (75° to 90°); when the action is finished the liquid is decanted from the sediment, which contains all the arsenic. On addition of water to the solution a white precipitate of basic nitrate falls, the constitution of which varies with the amount of water used. This was formerly known as *magistery of bismuth*, and is now called *flake* or *pearl white*, the latter name being also applied to the oxychloride of bismuth.

For pharmaceutical purposes the subnitrate is prepared as follows: Dissolve 2 parts of bismuth in 4 parts nitric acid of sp.gr. 1·42, diluted with 3 parts water, pour from deposit, if any, evaporate to one-third the bulk, and pour into 80 parts of water, filter, wash and dry the precipitate at a temperature not above 55°.

It is a pearly-white powder consisting of minute crystalline scales. It is employed as a flux for certain enamels, augmenting their fusibility without imparting any colour, and on this account is used as a vehicle for metallic oxides. For the colourless iridescent glaze on porcelain the basic nitrate is rubbed with resin and gently heated with lavender oil; by the addition of coloured oxides, yellow and other colours are produced. It is also used like the oxide and in the same proportions for gilding porcelain, and to some extent as a cosmetic under the names *blanc de fard* and *blanc d'Espagne*. It is largely used in medicine.

When prepared from impure metal it is liable to contain arsenic, lead, and silver; tellurium has also been suspected (Pharm. J. 3, No. 287). To test for arsenic, heat a little of the nitrate in a tube until brown fumes cease to be evolved. Add a small crystal of potassium acetate, and again heat; in presence of a trace of arsenic the odour of kakodyl is observed (A. Glenard, J. de Pharm. [4] 1, 217).

Bismuth chloride $BiCl_3$. This compound is produced when finely powdered bismuth is thrown into chlorine gas or when chlorine is passed over the heated metal. It is also formed by the solution of bismuth in *aqua regia* and evaporation of the liquid; or by distilling a solution of the oxide in hydrochloric acid, changing the receiver when all the water has distilled over.

It is a white, easily fusible solid, which absorbs moisture from the air, forming a crystalline hydrate. By the addition of water a white precipitate of basic chloride or oxychloride is produced corresponding to BiOCl, though its composition varies considerably.

The **oxychloride of bismuth** is, however, usually prepared by pouring a solution of the normal nitrate into a dilute solution of common salt, forming oxychloride of bismuth and sodium nitrate.

It is a white pearly powder known as *pearl white*, and is used as a pigment, and in the preparation of a very fine yellow pigment known as Merimée's antimony yellow (*v.* ANTIMONY). For double salts of bismuth chloride and chlorides of bivalent metals, *see* Weinland, Alber and Schweiger, Arch. Pharm. 1916, 254, 521.

Bismuth chromate *v.* under Chromium.

Bismuth sulphite, produced by the action of sulphurous acid on bismuth carbonate, or by double decomposition between a bismuth salt and an alkali sulphite, is a white crystalline powder, and is used in medical practice to check intestinal fermentation, and in cases of worms.

The **organic compounds** of bismuth have found many applications in medicine and surgery.

Bismuth salicylate is prepared, according to Causse (Compt. rend. 112, 1220), by adding a solution of a neutral salicylate to a solution of bismuth nitrate in a minimum amount of hydrochloric acid. Considerable quantities of ammonium chloride are added to the solutions before they are mixed. Hydrated bismuth salicylate $Bi(C_7H_5O_3)_3,4H_2O$ is thus obtained as a white crystalline powder, insoluble in cold water.

A better method of preparation, due to

Thibault (Bull. Soc. chim. 25, 794), consists in treating the bismuth oxide obtained by precipitation from 15 parts of bismuth nitrate with a solution of 10 parts of salicylic acid in 200 parts of water and heating on the water-bath till the action is complete. The product is decanted, washed with cold alcohol, and dried at 100°. It is thus obtained in rose-grey crystals, which are soluble without decomposition in cold alcohol, ether, or in a saturated aqueous solution of salicylic acid.

Martinotti and Cornelio (Bull. Chim. Pharm. 40, 141) point out that commercial preparations of the salt vary very much in composition, the amount of acid ranging from 5 to 67 p.c., and that of bismuth oxide from 37 to 79 p.c.

Kebler, however, has shown (Pharm. J. 64, 591) that the alcoholic test of the British Pharmacopœia is too stringent, as hot alcohol decomposes the salt. A more trustworthy method of testing of bismuth salicylate for free acid consists in extracting it with 90 p.c. benzene and filtering the extract into dilute ferric chloride solution (1 in 3000), when a violet ring is produced at the junction of the two liquids if free acid is present.

Basic bismuth gallate, known commercially as '*dermatol,*' is prepared as follows: 306 grams of basic bismuth nitrate is dissolved in 328 grams nitric acid of strength 38°B., diluted with 200 grams water. The solution is filtered through glass-wool, evaporated down to 600 grams, and allowed to crystallise. The product is dissolved in 980 grams glacial acetic acid, diluted with 8 litres of water, and then mixed with a solution of 188 grams crystallised gallic acid in 8 litres of water. The precipitate of bismuth gallate thus produced is washed five or six times with water, pressed, and dried (Hartz, Pharm. Rundsch. 12, 182).

Another method consists in treating a solution of bismuth nitrate in nitric acid with a solution of gallic acid in 70 p.c. alcohol, nearly neutralising with sodium hydroxide or sodium carbonate, and finally adding considerable quantities of sodium acetate or diluting largely with water. The compound is thus obtained as a yellow precipitate, which is collected and dried (Eng. Pat. 6234, 1891).

The empirical formula of the substance is $BiC_7H_7O_7$, and Thibault (J. Pharm. Chim. 14, 487) considers that it is really bismuthogallic acid, adducing in favour of this view the fact that with alkalis it forms salts of which potassium bismuthogallate $K_3BiC_7H_5O_7$ is a type.

A general method for the preparation of bismuth salts of organic acids is the solution of freshly precipitated bismuth hydroxide in a solution of the acid (Fischer and Grützner, Arch. Pharm. 1894, 232, 460; *v.* also Telle, *ibid.* 1908, 246, 484, for the preparation of *bismuth lactate* by this method).

Basic bismuth dibromohydroxynaphthoate, which has been suggested as a substitute for iodoform in surgical dressings (G. Richter, Apoth. Zeit. 1908, 23, 600), is obtained by a similar method. β-hydroxynaphthoic acid is brominated in acetic acid solution, and the recrystallised product heated with bismuth hydroxide. The salt is a finely crystalline, yellow, odourless, insoluble powder, which is unaffected by heating to 110°.

Bismuth chrysophanate ('*Dermol*')

$$Bi(C_{15}H_9O_4)_3 \cdot Bi_2O_3(?)$$

a yellowish-brown powder, is, according to Merck, a mixture of impure chrysarobin and bismuth hydrate.

Compounds of bismuth with phenols are obtained by double decomposition between an alkaline salt of the phenol and a salt of bismuth, such as the nitrate. Among those that have been made commercially may be mentioned:

orphol (the β-naphthol compound)

$$C_{10}H_7OBi(OH)_2+Bi_2O_3+H_2O\,;$$

xeroform (the tribromophenol compound)

$$(C_6H_2Br_3O)_2Bi \cdot OH+Bi_2O_3\,;$$

helcosol (the pyrogallate)

$$[C_6H_3(OH)_2O]_2 \cdot Bi \cdot OH.$$

An important pathological application of bismuth salts is their administration internally in order to outline parts of the body in Röntgen ray work.

Bismuth oxyiodosubgallate $C_6H_2(OH)_3 \cdot CO_2 \cdot BiI(OH)$, '*airol,*' is prepared by heating together in 50 parts of water 35 parts bismuth oxyiodide, and 18·8 parts gallic acid until the product is a greyish-green powder. It is used as a substitute for iodoform.

Other compounds of bismuth to which trade names have been given are:

Bismal, bismuth methylenedigallate, obtained by the general method from the hydroxide and methylenedigallic acid.

Markasol, bismuth borophenate.

Thioform, bismuth dithiosalicylate, used as a substitute for iodoform (*v.* SYNTHETIC DRUGS).

Tertiary aromatic bismuthines and their halogen derivatives have been prepared by Challenger (Chem. Soc. Trans. 1914, 105, 2210). Other organo-bismuth compounds have been described by Löwig, Annalen, 1850, 75, 355; Breed, *ibid.* 1852, 82, 106; Dunhaupt, *ibid.* 1854, 92, 371; Michaelis and collaborators, Ber. 1887, 20, 52, 54, 1516; 1888, 21, 2035; Gillmeister, Ber. 1897, 30, 2843; Pfeifler and Pietsch, *ibid.* 1904, 37, 4620; Hilpert and Grüttner, *ibid.* 1913, 46, 1685; Hilpert and Ditmar, *ibid.* 3741; Ehrlich and Karret, *ibid.* 3564; Vanino and Mussgnug, Ber. 1917, 50, 21.

BISMUTHINITE or **BISMUTH-GLANCE.** Native bismuth sulphide, Bi_2S_3, occurring as acicular or bladed orthorhombic crystals or lamellar masses, very like stibnite (Sb_2S_3) in appearance. In Queensland and Bolivia it is found in sufficient abundance to be mined as an ore of bismuth. L. J. S.

BISMUTITE. Basic bismuth carbonate, containing about 90 p.c. Bi_2O_3; formula perhaps $Bi_2O_3 \cdot CO_2 \cdot H_2O$. It is a yellowish earthy material, and presenting such an appearance is surprisingly heavy (sp.gr. variously given as 6·9 and 7·6). It occurs as an alteration product of native bismuth, and in Bolivia is an important ore of this metal. L. J. S.

BISMUTOSE *v.* SYNTHETIC DRUGS.

BISTRE *v.* PIGMENTS.

BISULPHIDE OF CARBON *v.* *Carbon disulphide*, art. CARBON.

BITTER ALMOND OIL *v.* BENZALDEHYDE, and OILS, ESSENTIAL.

BITTER APPLE *v.* COLOCYNTH.

BITTER SWEET *v.* DULCAMARA.

BITTER WOOD *v.* QUASSIA.

BITTERN. The mother liquor which remains after the crystallisation of common salt from sea-water, or the water from salt springs. It contains soluble magnesium salts, bromides, and iodides.

The same term is also applied to a mixture of equal parts of quassia extract and sulphate of iron, 2 parts extract of *Cocculus indicus*, 4 parts Spanish liquorice, and 8 parts treacle, used to sophisticate beers.

BITUMEN. This term includes a considerable number of inflammable mineral substances consisting mainly of hydrocarbons. They are of various consistence, from thin fluid to solid, but the solid bitumens are for the most part liquefiable at a moderate heat. The purest kind of fluid bitumen, called naphtha or rock oil, is a colourless liquid of sp.gr. 0·7–0·84, and with a bituminous odour. It often occurs in nature with asphalt and other solid bitumens. Petroleum is a dark-coloured fluid variety containing much naphtha. Maltha or mineral tar is a more viscid variety. The solid bitumens are *asphalt* (*q.v.*); *mineral tallow* or *hatchetin*; *elastic bitumen*, *mineral caoutchouc* or *elaterite*; *ozokerite*, &c.

An abundance of bitumen is found in the island of Trinidad at the Pitch Lakes, and in Mexico. It is supposed to be a product of the decomposition of vegetable matter, and consists chiefly of hydrocarbons with variable quantities of oxygen and nitrogen (*v.* PITCH).

BITUMINOUS COAL *v.* FUEL.

BIXEIN, BIXIN. Colouring matters of annatto (*v.* ANNATTO).

BLACK BAND IRONSTONE *v.* IRON, ORES OF.

BLACKBERRIES. The fruit of the bramble, *Rubus fruticosus*. König gives, as the average composition:

Water	Protein	Free acid	Sugar	Other carbohydrates	Fibre	Ash
86·4	0·5	1·2	4·4	1·8	5·2	0·5

The seeds contain about 12·6 p.c. of a drying oil, sp.gr. at 15° 0·9256, iodine number 147·8, the liquid fatty acids—about 91 p.c. of the oil, contain about 80 p.c. of linolic acid, 17 p.c. of oleic acid, and 3 p.c. of linolenic acid, whilst the solid acids, chiefly palmitic acid, amount to about 4·7 p.c.; volatile acids are not present in the oil. A small quantity of phytosterol is present (Krzizan, Chem. Rev. Fett u. Harz, Ind. 1908, 15, 7). For a study of the colouring matter of the fruit, *see* Vecchi (Chem. Zeit. 1914, i. 1209). H. I.

BLACK BOY GUM *v.* BALSAMS.

BLACK CHALK. A kind of clay containing carbon, found in Carnarvonshire and in the Isle of Islay.

BLACK COPPER *v.* COPPER.

BLACK EARTHY COBALT *v.* COBALT.

BLACK FLUX *v.* ASSAYING.

BLACK HAW. The dried bark of *Viburnum prunifolium* (Linn.).

BLACK HELLEBORE ROOT. *Radix Hellebori nigri.* (*Racine d'Ellebore noir*, Fr.; *Schwarze Nieswurzel*, Ger.).

The root of the *Helleborus niger* (Linn.) or Christmas Rose (Woodville, Med. Bot. 169; Bentl. a. Trim. 2). Black hellebore and the nearly related green hellebore, *Helleborus viridis* (Linn.), are seldom employed in England except in veterinary medicine. They are both powerful intestinal irritants. (*Veratrum viride* and *V. album*, also known as green and white hellebore respectively, are very different plants, and contain alkaloids.)

According to Husemann and Marmé (Annalen, 133, 55), both species of *Helleborus* contain a glucoside *helleborein*, and a smaller quantity of a second glucoside *helleborin*. The former is, according to Sieburg (Arch. Pharm. 1913, 251, 154), an amorphous saponin $(C_{21}H_{34}O_{10})x$, and is hydrolysed by boiling dilute sulphuric acid to 2 mols. each of dextrose and arabinose, [illegible] mol. of acetic acid, *acid helleboretin* $C_{21}H_{36}O_7$ (a lactone ?), and *neutral helleboretin* $C_{15}H_{24}O_3$, a greenish-black mass. Helleboreïn is not a suitable substitute for digitalis (*cf.* also Thaeter, Arch. Pharm. 1897, 235, 414). Helleborin melts with decomposition at 150°, dissolves easily in boiling alcohol or chloroform and gives a deep red solution with sulphuric acid.

BLACKING. Blacking for shoes is mentioned as early as 1598, but it was not introduced into England until the reign of Charles II. It consists of (1) black bone charcoal (free from calcium phosphate, otherwise it is subsequently treated with dilute sulphuric acid) and black colouring matter; (2) a mixture of sugar and oil, which, on rubbing, imparts the gloss; and (3) fatty matter for preservation purposes.

Carnauba wax with its hardness and high melting-point is the basis of modern friction polishes. The cheaper candelilla wax may, to a certain extent, replace the carnauba with but little difference in the quality of the polish.

There are two chief methods for working these waxes into polish: The wax is emulsified by boiling in a solution of borax. The product is known as white stock. If polish is to be in the form of paste, the white stock while hot is mixed with a hot solution of ordinary laundry soap and sufficient nigrosin to give the desired depth of colour. The mixture cools as a soft paste that may readily be applied by means of a brush or sponge. If the polish is desired in the liquid form, the best grade of Castille soap is used; a solution of this variety of soap does not gelatinise. Numerous trials have shown that no matter how dilute the soap solution, a satisfactory liquid cannot be obtained unless Castille soap is used. Both the paste and liquid forms are widely used. With a moderate friction, the hard waxes held upon the leather by the soap, give a beautiful and very desirable polish.

The second method of dealing with the hard waxes is as follows: Carnauba or candelilla or a mixture of the two with beeswax and ceresin or paraffin is dissolved in hot turpentine and mixed with very finely pulverised bone charcoal. When properly cooled there results a firm paste that spreads rapidly under a brush or sponge. When this mixture is poured into boxes it must be properly cooled, otherwise there is a separation of the harder waxes from the solvent, the result being a granular sloppy mass instead of the firm paste desired. If the harder waxes alone were used it would be difficult to prevent separation from the turpentine on cooling, hence the admixture of softer waxes. Beeswax gives also a toughness or lack of shortness to the paste, and a smooth finish that cannot be obtained without it. These softer waxes reduce the gloss available from the carnauba or candelilla. The use of bone black as a colouring agent is an attempt to overcome the weakness inherent in the use of the softer waxes, and to add to the gloss obtainable from the waxes that obtained by friction of the bone carbon.

For tan leathers the same goods are used, except that a brown or yellow dye and pigment replace the nigrosin and bone char. The application of the tan polish is frequently preceded by the use of a cleaning solution to remove stains and discolouration (J. T. Donald, J. Soc. Chem. Ind. 1913, 32, 459).

A liquid blacking can be prepared from 120 parts of ivory black, 90 parts brown sugar, 15 parts olive oil, and 500 parts stale beer. The ivory black, sugar, and olive oil are mixed into a smooth paste, and the beer added under constant stirring (Hiscox, 1907).

A German recipe is as follows: 25 parts Marseilles soap are dissolved in 375 parts of warm spirit (25 p.c.) and 40 parts of glycerol added; this is shaken and added to a solution of 200 parts of shellac dissolved in 1000 parts of spirit (95 p.c.) and 5 parts nigrosine in 125 parts of spirit added. The mixture is well shaken in a closed vessel and left for a fortnight.

Liquid polish. 4 oz. asphaltum, 8 fl. oz. turpentine, 3 fl. oz. of gold size. ¼ oz. nigrosine, and 3 fl. oz. linseed oil. The mixture is heated until uniform and thinned down to desired consistence with oil of turpentine (Phot. J. Dec. 1908, 738).

Day and Martin's chief blacking is obtained by mixing ground animal charcoal, sperm oil, raw sugar or treacle, and a small portion of vinegar. Dilute sulphuric acid is then added to the mass until intumescence ceases, and the product is thinned by the addition of vinegar.

Bryant and James's indiarubber blacking is prepared by triturating thoroughly 18 oz. very fine shreds of indiarubber, 9 lbs. hot rapeseed oil, 60 lbs. finely powdered animal charcoal, 45 lbs. treacle, 1 lb. gum arabic previously dissolved in 20 gall. vinegar. The whole is placed in a wooden vessel, and 12 lbs. sulphuric acid added in small quantities at a time, and stirred for ¼ hour daily for 14 days, 3 lbs. of finely ground gum arabic added, and stirring continued for 14 days. If required in the paste form, only 12 gall. vinegar added and 6 or 7 days' stirring is sufficient.

Brunner makes a blacking by stirring 10 parts of bone black with 100 parts of glucose syrup, and 5 parts sulphuric acid added with rapid stirring until the mass is homogeneous. 2 parts of soda are dissolved in 4 parts water, and 20 parts train oil added and boiled with constant stirring until a thick liquid is formed: the other mixture is then added with repeated stirring.

A cheap and good shoe blacking may be prepared by mixing 1 lb. of ivory black, 1 lb. molasses, 8 tablespoonfuls sweet oil, and 1 oz. of gum arabic, dissolved in 2 quarts of vinegar and ½ lb. of oil of vitriol.

Paste blacking. Mix 16 oz. ivory black, 16 oz. lampblack, 6 oz. treacle, 5 oz. vinegar, and 4 oz. sperm oil. Mix and add gradually 4 oz. sulphuric acid. When intumescence ceases, add ½ oz. of iron sulphate, 6 oz. gum arabic, and 5 oz. water (Pharm. Formulæ, 1908, 378).

Sticks of blacking of plastic consistence are made from the following: 5 oz. stearin, 5 oz. paraffin wax, 2½ oz. carnauba wax, 2½ oz. lustrous pitch, and 7 oz. turpentine (Pharm. J. Pat. 2564, 1908).

Hiscox describes the following paste: 122 parts Marseilles soap, 61 parts potassium carbonate, 500 parts beeswax, and 2000 parts water are mixed with constant stirring and 153 parts rock candy (powdered), 61 parts gum arabic, and 1000 parts ivory black are added with constant stirring.

Boot polish. 5½ oz. ozokerite, 2 lbs. cerasin, 5½ oz. carnauba wax, 1¾ oz. beeswax, 4 pints turpentine, 2 lbs. lampblack, 20 grams black aniline dye, and perfume added if desired (Pharm. J. 1908, 506).

Self-shining blacking. Dissolve 4 oz. gum arabic, 1½ oz. coarse sugar, ¼ pint good black ink, and 1 oz. sweet oil, rub in a mortar, add 2 oz. strong vinegar, and add lastly 1 oz. rectified spirits (Scientific Amer. 1903, 39).

French shoe dressing. 32 oz. vinegar, 8 oz. logwood, and ¼ oz. potassium dichromate are boiled and strained whilst hot into a mixture of 4 oz. gelatine, 4 oz. tragacanth, 4 oz. glycerol and 15 oz. water. The mixture is allowed to stand for some hours: 2 oz. indigo are then added, and the whole triturated in a mortar (Pharm. Form. 1908)

Boot-top liquid. 1 oz. oxalic acid, 1 oz. zinc sulphate, dissolved in 30 oz. water. Apply with a sponge to the leather, which has been previously washed with water, then wash off with water, and dry (Workshop Receipts, 1909, 123).

For kid shoes. 2 oz. gum shellac, 1 oz. aqueous ammonia, 8 oz. water, and aniline black enough to colour. The first two ingredients are heated almost to boiling, and water is added to make the whole measure 16 oz. (Scien. Amer. 1903, 39).

Waterproof blacking. 6 oz. caoutchouc and 3 lbs. hot rape oil are added to 20 lbs. ivory black, 15 lbs. molasses, and 6 or 7 gall. vinegar in which 6 oz. ground gum arabic has been dissolved; then add 4 lbs. sulphuric acid and stir constantly. Allow to stand for 2 weeks, then add 1 lb. fine gum arabic. Stir daily during 2 weeks, and bottle (Workshop Receipts, 1909, 124).

For *dress boots.* 8 oz. gum arabic and 2 oz. molasses dissolved in 2 oz. ink and ¼ pt. vinegar. This is strained, and 2 oz. spirits of wine added.

BLACK-JACK. A miner's term for blende, or zinc sulphide (*v.* ZINC). *V.* ZINCBLENDE.

BLACK LEAD. The common name of plumbago or graphite (*v.* CARBON).

BLACKLEY BLUE *v.* INDULINES.

BLACK LIQUOR. Ferrous acetate (*v.* ACETIC ACID).

BLACK MUSTARD SEED OIL *v.* RAPE OIL; OILS and FATS.

BLACK TELLURIUM *v.* TELLURIUM.

BLACK TIN *v.* TIN.

BLACK VARNISH or **BLACK JAPAN** *v.* VARNISH.

BLACK WAD *v.* MANGANESE.

BLACK, WOOL. *v.* AZO- COLOURING MATTERS.

BLANK FIXE. Trade name for ground barium sulphate used as a pigment (*v.* BARYTES).

BLANKIT. A trade or factory term for sodium hydrosulphite.

BLANQUETTE. A kind of crude soda, less caustic than barilla, obtained at Aigues-Mortes by the incineration of *Salsola kali*.

BLAST FURNACE GAS *v.* FUEL.

BLASTING GELATINE AND POWDER *v.* EXPLOSIVES.

BLAU or **BLUE GAS.** A mixture of volatile hydrocarbons, *e.g.* propane, butane, the pentanes, &c., containing hydrogen and methane, &c., in solution under pressure. The pressure solution is filled into steel cylinders, and is thus available for transport. Used for illuminating, heating, and power purposes (Hallock, J. Soc. Chem. Ind. 1908, 550).

BLEACHING. This term signifies the art of destroying the natural colour of vegetable and animal products in such a manner as to leave them unimpaired with as white an appearance as possible. The removal of certain other natural or artificial impurities usually accompanies the bleaching proper. The art acquires its greatest importance in connection with the textile fibres, cotton, linen, wool, and silk; hence special reference will be made to the modern methods of bleaching these materials.

Cotton bleaching. Cotton is usually bleached in the form of yarn, thread, and fabric, seldom as loose cotton-wool. The natural impurities occurring in raw cotton amount to about 5 p.c., and consist chiefly of pectic matters; other substances present are brown colouring matter and very minute quantities of a fatty acid, cotton wax, and albuminous matter. The soiled grey appearance of raw cotton-wool, yarn, and thread is almost entirely due to the presence of these natural impurities. Cotton cloth or calico, however, is still further contaminated with flour or starch, fatty matter, China clay, and other mineral substances, all of which, to the amount of 30–50 p.c., have been introduced during the sizing of the warp.

Cotton yarn and thread bleaching. If the cotton yarn is in the form of 'warps,' these are loosely plaited by hand or machine in order to reduce their inconvenient length; if in the form of 'hanks,' these are bleached separately or linked together in chain form; weft yarn is sometimes bleached in the form of 'cops,' *i.e.* ready for the spool of the weaver's shuttle.

The several operations of the bleaching process for 1500 kilos. yarn, employing low pressure kiers, are as follows:—

1. *Ley-boil.* 300 litres caustic soda (sp.gr. 1·16), 2000 litres water, boil 6 hours; wash in kier 1 hour.
2. *Chemicking.* Bleaching-powder solution (sp.gr. 1·005), steep under sieve 2 hours; wash under sieve half an hour.
3. *Souring.* Sulphuric acid (sp.gr. 1·005), steep under sieve half an hour; wash under sieve half an hour and afterwards in washing machine.
4. *Soaping and blueing.* Soap solution about 6 grams per litre, with addition of small quantity of indigo-purple (indigotin monosulphonate of soda), steep 2 hours under sieve.
5. *Dumping.* Pass through dumping machine containing soap solution and indigo-purple, as in operation No. 4; wash, squeeze or hydro-extract, and dry.

The first, second, and third operations are repeated in the case of thread because of its closer texture. For the second ley-boil, 30 litres caustic soda (sp.gr. 1·16) and 15 kilos. soap are used; the chemicking and souring are exact repetitions.

The *ley-boil* takes place in large iron boilers or 'kiers,' a representation of which is shown in Fig. 1.

The boiler A has a central puffer pipe, B, furnished with a bonnet or spreader, M, at the top.

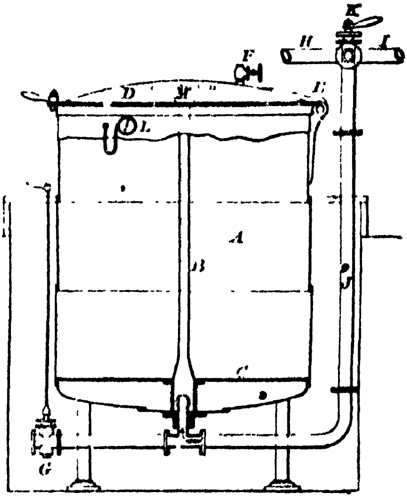


FIG. 1.

C is a perforated false bottom; D is the lid hinged at E and capable of being readily lifted by means of a chain and counterweight; F is an air valve, L a steam pressure gauge; H and I are the steam and liquor pipes connected by the two-way valve K with the pipe J, which enters the kier immediately below the puffer pipe; G is the let-off valve.

When such a kier has been charged with yarn and caustic soda solution, the lid is fastened down and steam is admitted. The liquor below the false bottom soon begins to boil, and as the pressure of steam increases, a portion of the boiling liquor is forcibly ejected up the puffer pipe and spread over the yarn. The liquor drains through the yarn, soon to be ejected as before. In this intermittent manner the circulation of the boiling liquor is maintained.

The apparatus for chemicking, souring, washing under sieve, soaping and blueing, shown in Fig. 2, consists of a stone tank, E, with perforated false bottom F, and communicating by the valve G with the stone tank D below. The chain of yarn is drawn from the kier and led into the tank E by means of the winch A. When E is suitably filled with yarn, the liquor in tank D is raised by the pump C to the sieve F', whence it drains through the yarn into the well below, again to be pumped up as before; B is the eccentric wheel on revolving shaft by which the pump is worked.

The 'dumping' machine referred to consists of a pair of heavy wooden rollers placed over a large wooden tank containing the soap solution. The upper roller is covered with cotton rope and rests loosely on the lower one. The yarn is first passed through the soap solution and then between the squeezing rollers; the irregularities caused by the linking or plaiting impart to the upper roller a constant jumping motion, which thus effectually cleanses the yarn and presses the soap and blue into the fibres.

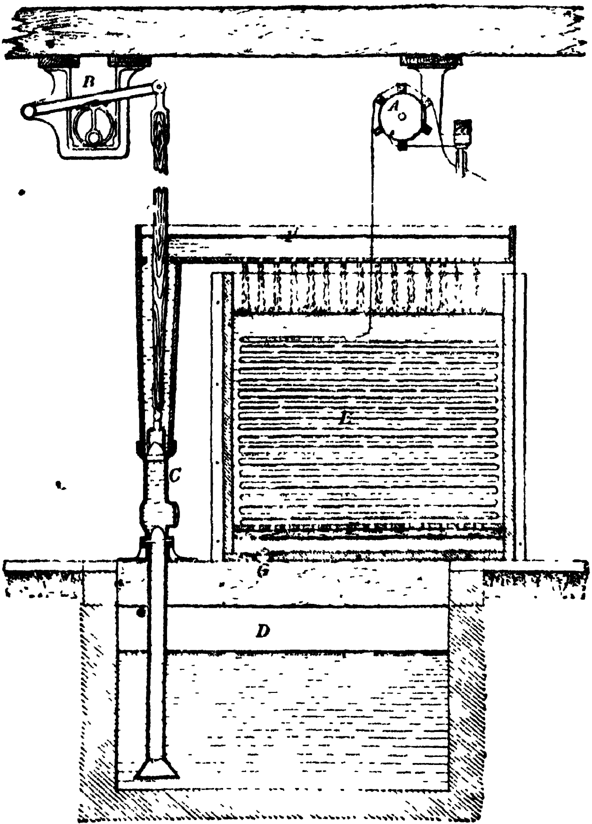


FIG. 2.

When hank yarn is not linked to form a chain, but treated as separate hanks, 'wash stocks' in which the yarn is subjected to the beating action of heavy wooden hammers replace the dumping machine.

Bleaching of yarn in the form of 'cops' or 'cross-wound spools' ('cheeses'). The cops may be packed in wicker baskets or in linen bags and boiled in an ordinary kier, or they are treated in special cop-dyeing apparatus. It is preferable to use a solution of sodium hypochlorite in place of a bleaching-powder solution.

Cotton-cloth or calico bleaching. According to the purpose for which the bleached material is intended, we may distinguish between the *madder bleach*, the *market bleach*, and the *Turkey-red bleach*.

The madder bleach. This, the most thorough kind of calico bleaching, is in general use with calico-printers. It aims at entirely removing every impurity which will attract colouring matter in the madder or other dye-bath, so that the finished print may have a pure white ground.

Before proceeding to the actual bleaching process the preliminary operations of *stamping*, *stitching*, and *singeing* have to be performed.

To recognise each piece of cloth and to trace damages, the ends are stamped with numbers and letters, usually with thick gas tar, occasionally with aniline black. The pieces are then stitched together by machine.

The *singeing* operation is for the purpose of burning off the loose fibres on the surface of the calico, since they interfere with the production of fine impressions, and are apt to give rise to certain defects during the printing process. It is performed by rapidly passing the cloth in the open width over red-hot copper plates or cylinders, or over a row of Bunsen gas flames. We may distinguish, therefore, between *plate singeing* and *gas singeing*, the former being generally preferred for thick heavy cloth, the latter for light thin cloth, muslins, &c.

In plate singeing it is important that the plates be kept at a uniform strong red heat sufficiently high to overcome the cooling action of the rapidly moving cloth. The best results are obtained by means of the 'singeing roller,' which consists of a slowly revolving copper cylinder through which a furnace flame is conducted. In this case the cloth presses continually against a different portion of the red-hot surface of the roller; the cooling action is thus reduced to a minimum, and a regular even singe is the result.

All singeing machines are provided with lever arrangements for immediately removing the cloth from the hot plate, or the gas flame from the cloth, in case of necessity; further danger from fire is avoided by causing the singed cloth to pass at once between a pair of rollers moistened with water, or through a small steam chamber, in order to extinguish sparks adhering to the cloth.

The above preliminary operations are now succeeded by those of the bleaching proper. The following is an outline of the process at present in use for 24,000 kilos. cloth, employing ow-pressure kiers :—

1. Wash after singeing.
2. *Lime-boil.* 1000 kilos. lime, water about 37,000 litres ; boil 12 hours ; wash.
3. *Lime sour or grey-sour.* Pass through hydrochloric acid (sp.gr. 1·01) ; wash.
4. *Ley-boils.* 1st. 340 kilos. soda ash, water about 37,000 litres ; boil 3 hours.
   2nd. 860 kilos. soda ash, 380 kilos. resin, 190 kilos. caustic soda (solid), water 37,000 litres ; boil 12 hours.
   3rd. 380 kilos. soda ash, water 37,000 litres ; boil 3 hours ; wash.
5. *Chemicking.* Pass through bleaching-powder solution (sp.gr. 1·0025) ; pile 2–12 hours ; wash.
6. *White-sour.* Pass through hydrochloric or sulphuric acid (sp.gr. 1·01) ; pile 1–3 hours.
7. Wash, squeeze, open out, and dry.

1. *Wash after singeing.* From the singeing house the cloth is passed through the washing machine in rope form, then plaited down on the floor and allowed to lie 'in pile' for some hours to soften. By this operation the cloth is well soaked with water, and is thus better prepared to absorb the liquors used in the subsequent operations. Should the cloth be heavily sized, much of the adventitious matter is also removed at this stage.

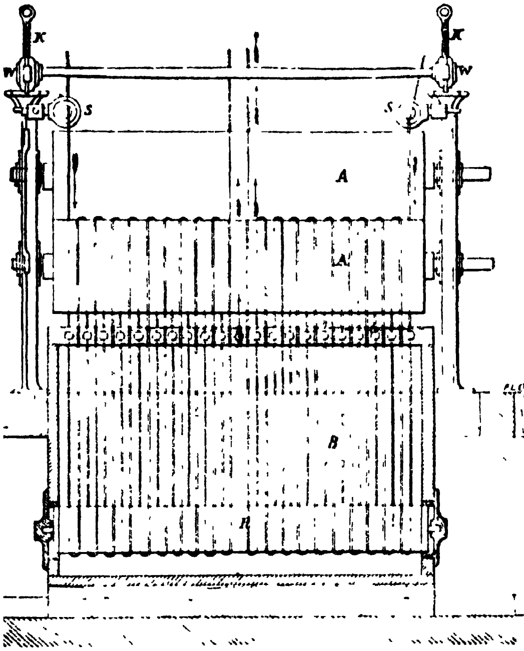


FIG. 3.

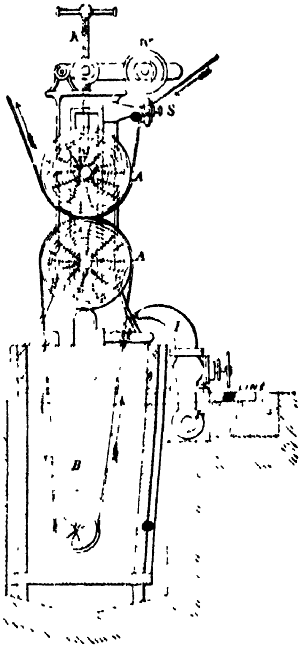


FIG. 4.

The form of washing machine generally employed is shown in Figs. 3 and 4. It consists of a water trough, B, above which a pair of heavy wooden squeezing rollers, A, A, are supported. Two strands of cloth are washed simultaneously ; they enter the machine at the ends, pass between the squeezing rollers, then round the roller R in the water trough, again between the rollers A, A, and thus travel spirally towards the centre of the machine, whence they are drawn out by a winch and piled on the floor. A constant stream of water from the main D enters at the centre of the trough by the tap E, the dirty water flowing out at both ends ; C, C are wooden guide pegs to separate the several strands of cloth ; S, S are strong brass rings or 'pot eyes' through which the cloth enters the machine, and which can be set at any angle to regulate its tension ; K and W are the screws, levers, and weights for regulating the pressure of the squeezing rollers against each other. The action of this machine is such that the cloth is continuously being soaked with water and then squeezed, thus causing a vigorous stream of water to flow down the upward-moving strands of cloth.

2. *Lime-boil* (lime-bowk, bucking, bowking). The pieces are run through milk of lime supplied to a washing machine of small dimensions—generally termed the 'liming machine'—and are at once drawn by winches into the lime kiers, carrying with them the lime they have absorbed. The cloth is plaited in regular folds and well tramped down by boys, who enter the kiers.

After adding the necessary amount of water, the boiling and circulation of the liquor takes place as already described in the case of the ley-boil of cotton-yarn bleaching.

The lime-boil has for its object the decomposition of the fatty, waxy, and resinous impurities present in the cloth. Though not removed, but adhering still to the fabric in the form of lime-soaps, their altered condition facilitates their removal by the subsequent processes. The starch of the size is removed, and the colouring matter of the fibre is modified. Lime is preferred to caustic soda because it is cheaper, and much more effective in saponifying neutral fatty matter than the caustic or carbonated alkalis; indeed, with the exception of barium hydroxide, it seems to be the most energetic saponifying agent which could be used in cotton bleaching.

It is very essential to have a sufficiency of water in the kier, so that it stands at least about 2 feet above the false bottom; otherwise the cloth, either at the top or bottom of the kier, is very apt to be tendered, probably because it becomes oxidised by the action of the steam upon the cloth in its limed condition. On the other hand, an excess of water in the kier is to be avoided, since then the cloth is apt to float and become entangled, or damaged by rubbing against the sides of the kier during the boiling. When closed high-pressure kiers and live steam are employed, the increase in volume of liquor by the condensation of the steam must be taken into account, and, if necessary, a little liquor must be allowed to escape.

Of the several varieties of kier which have from time to time been introduced in practice, mention may be made of '*Barlow's kiers*.' These are always worked in pairs, and so arranged that the top of one kier is connected by a pipe with the bottom of the other; the pipes which enter at the top and centre of each kier are continued as perforated pipes or 'distributors' to a little above the false bottom, and then to the bottom of the kier as a stay. Both kiers having been charged with cloth, the necessary amount of water is run into one kier only; high-pressure steam is then admitted at the top, and the liquor forced out below enters the distributor of the other kier at the top and permeates the cloth. When all the liquor has been thus transferred, the taps are reversed so that the steam forces the liquor in a similar manner back into the first kier. This alternating process and circulation of the liquor is continued for about seven hours.

Pendlebury's arrangement of kiers is precisely similar to that of Barlow, the only difference being that one kier is smaller and serves only to hold the liquor each time it is forced through the cloth contained in the larger kier. The arrangement is cheaper, more economical as regards space required, and is suitable for small requirements.

In the *vacuum kier* of Mason and others, the circulation of the liquors is effected by means of a pump. After filling the kier with cloth, the air is pumped out and the boiling liquor is then admitted; in this manner a more perfect penetration of the material by the liquor is obtained.

The *injector kier* of Mather and Platt is shown in Fig. 5. A is the kier filled with cloth; B, B are the steam pipes; C is the injector; and D the circulating pipe; F is the liquor pipe by which water or other liquor is admitted; E, E is the draw-off valve and waste pipe. When the kier has been suitably filled with cloth and liquor, steam is turned on, and, by the action of the injector C, the liquid is withdrawn from the kier below, forced up the pipe D, and spread over the cloth at G. Temporarily collecting at H, the liquor is gradually drawn through the cloth, and in this manner a continual circulation of liquor is maintained.

3. *Lime-sour* (grey-sour). After the lime-boil the pieces are washed, then passed through a washing machine fed with dilute hydrochloric acid, and, if convenient, at once washed.

The object of the lime-sour is to decompose the insoluble lime-soaps fixed on the cloth during the lime-boil, and to dissolve and remove the lime, also any iron or other metallic oxides present. Experiments by A. Scheurer show also that the use of the lime-sour makes it less essential that complete saponification of the fatty matter should take place during the lime-boil than would be the case if it were omitted. This is so because the free fatty acid liberated during the lime-sour greatly facilitates the saponification of any undecomposed neutral fat during the succeeding ley-boil, since the soap which the fatty acid then forms emulsifies the neutral fat and exposes it to the action of the alkali employed. Hence the adoption of the lime-sour is equivalent to shortening the time of the lime-boil. A continual flow of fresh dilute acid into the machine must be maintained, and, since it is rapidly neutralised by the lime, it is well to ensure a constant slight acidity of the liquor by occasionally making acidimetrical tests. Hydrochloric acid is preferred to sulphuric acid, because it gives the more soluble calcium chloride. The soured cloth should never be permitted to remain long exposed to air, especially air currents, otherwise the acid is apt to concentrate in the exposed portions and thus tender the fibre.

4. *Ley-boil.* This operation takes place in the same kind of kiers as are used for the lime-boil. The fatty acids resulting from the decomposition of the lime-soaps during the grey-sour, also the brown colouring matters, are removed during this operation. Its special feature is the use of resin-soap, which greatly facilitates the removal of fatty matter by exercising a purely mechanical emulsive action, the alkali present being then able more readily to saponify the emulsified fats, particularly those neutral fats which perchance have escaped the action of the lime-boil. Ordinary soft-soap acts in a similar manner, but resin-soap is cheaper and better. A. Scheurer finds by experiment that, after caustic lime, the most rapid saponification of a neutral fat spotted on a piece of calico is effected when boiling under pressure at 120° C., by a solution containing 10 grams anhydrous caustic soda and 2½ grams resin per litre. Increasing the amount of resin does not hasten saponification, though this is done by increasing the velocity of the circulation of the solution. Indeed, *with circulation* even a more rapid saponification is effected with caustic soda and resin than with lime.

The preliminary short boiling with soda ash, which is sometimes replaced by merely soaking the cloth in a weak solution of soda ('sweetening'), prevents tendering of the cloth by neutralising any traces of acid left in by reason of insufficient washing after souring. The boiling with soda-ash after the resin-boil is for the purpose of completing the removal of fatty matters and any undissolved resin, which otherwise give rise to brown stains. Immediate removal of the cloth from the kier and washing is necessary to prevent the production of iron stains.

5. *Chemicking.* The application of the bleaching-powder solution takes place in washing machines of the ordinary kind, but provided with stone instead of wooden troughs, because of their greater durability. The bleaching action takes place essentially during the lying-in-pile or exposure to air of the cloth saturated with the solution of bleaching powder, the carbonic acid of the air liberates hypochlorous acid, and this, in the presence of the fibre, at once decomposes, yielding hydrochloric acid and oxygen: in the moment of its production the oxygen oxidises and destroys the traces of colouring matter present in the fibre, thus giving it the highest degree of whiteness.

It is necessary to avoid the use of strong solutions of bleaching powder, otherwise the fibre itself is attacked, oxycellulose being produced; and even if the cotton is not tendered thereby it is still apt to acquire brown stains during subsequent operations employed by the calico-printer, *e.g.* steaming, or to produce uneven shades in dyeing.

6. *White-sour.* This operation is similar to the lime-sour already described, except that sulphuric acid is usually employed instead of hydrochloric acid, chiefly because of its lower cost. Its object is to decompose and remove traces of undecomposed bleaching powder, lime, iron, and the oxidised colouring matter.

7. The *final washing* must be as thorough as possible in order to ensure the removal of all traces of acid, which, if left in the cloth, would inevitably tender portions of it during the drying process. After washing, the cloth is specially squeezed by passing through a pair of heavy wooden rollers, or through the modern grooved brass roller and disc machine of W. Birch. The chain of cloth then passes in a horizontal, loosely hanging position, between a pair of rapidly revolving, double-armed winches or scutchers, which effectually shake out the twist from the strand. Thus opened out to the full width, the cloth is dried by passing over steam-heated copper cylinders, and folded. The time usually required to complete the madder bleach is four to five days.

The market bleach. In market bleaching the object is simply to give a brilliant white appearance to the calico or other similar material, to fit them for immediate sale in the market as finished white goods. It is not necessary to have the calico 'well bottomed'—*i.e.* cleansed from all colour-attracting impurities, since no subsequent dyeing or printing is intended. The operations are for the most part identical with those of the madder bleaching process. The modifications introduced are shown in the following outline of the process, intended for 24,000 kilos cloth, employing open or low-pressure kiers:—

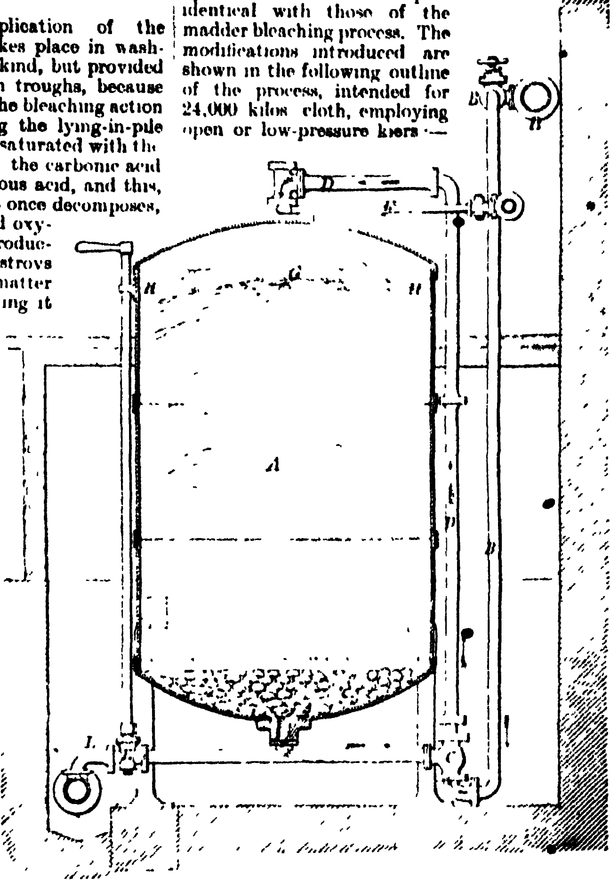


Fig 5

1. *Lime-boil.* 1440 kilos lime, water about 37,000 litres, boil 12 hours; wash.
2. *Lime-sour.* Hydrochloric acid (sp gr. 1·01); steep 2-4 hours; wash.
3. *First ley-boil or grey-boil.* 240 kilos. caustic soda (solid), about 37,000 litres water; boil 12 hours; wash.
4. *Chemicking.* Bleaching powder solution (sp.gr. 1·005); steep 2-4 hours; wash.
5. *Second ley-boil or white-boil.* 240 kilos. soda ash, about 37,000 litres water; boil 12 hours; wash.

6. *White-sour.* Sulphuric acid (sp.gr. 1·01); steep 2–4 hours; wash.
7. *Tint* with blue; squeeze dry.

More or less elaborate finishing operations follow—*e.g.* starching, calendering, beetling, stentering, &c. Some bleachers introduce a white-sour between operations 4 and 5, and a second chemicking between operations 5 and 6. The absence of resin-soap in the ley-boils is characteristic.

The Turkey-red bleach. This is merely a curtailment of the foregoing processes, and is specially intended for yarn or cloth to be subsequently dyed plain alizarin-red or Turkey-red. In it the operation of singeing and the application of bleaching powder are omitted, since they diminish the fulness and brilliancy of the Turkey-red dye; the use of the latter is to be avoided, because it gives rise to the production of oxycellulose. The use of resin-soap is unnecessary, and the process is limited to the following operations:—

1. Wash.
2. Boil in water 2 hours; wash.
3. *Ley-boils.*
   1st. 90 litres caustic soda (sp.gr. 1·35), about 3000 litres water; boil 10 hours; wash.
   2nd. 70 litres caustic soda (sp. gr. 1·35); ditto, ditto.
4. *Sour.* Sulphuric acid (sp.gr. 1·01); steep 2 hours.
5. Wash well and dry.

The above quantities of materials are intended for 2000 kilos. cloth, with low-pressure kier

The steamer-kier bleaching process. The bleaching processes previously described have been in vogue with little change during the last forty years; minor modifications have certainly been introduced, but the chief improvements have always been in respect of the mechanical appliances employed.

In 1883 Thompson patented a bleaching process in which the goods contained in an air-tight kier are submitted to the action of bleaching-powder solution and of carbonic acid alternately.

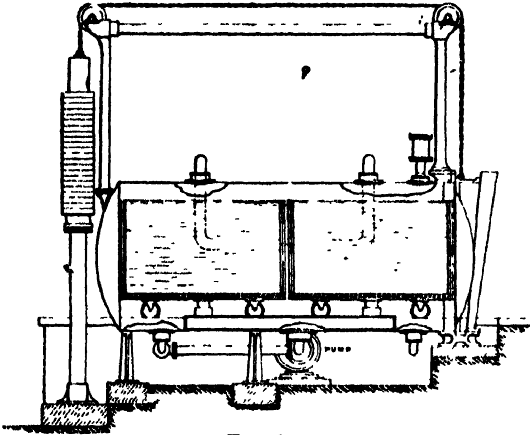


FIG. 6.

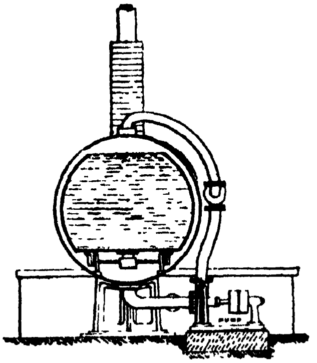


FIG. 7.

In 1884 W. Mather, of the firm of Mather & Platt, Manchester, devised an improved arrangement in which the calico could be passed continuously through chambers or tanks containing the two necessary agents mentioned.

The so-called *Mather-Thompson* process results from a combination of the two processes here indicated. With regard to the principles of the process there is nothing new, for the application of carbonic acid in connection with bleaching-powder solution was patented by P. F. Didot in 1855, while the steaming of goods impregnated with alkali was patented as far back as 1800 by J. Turnbull.

The novelty consists essentially in the machinery employed, by which the duration of the bleaching process is very much shortened, and other material advantages are gained.

In the following year Mather introduced the so-called *steamer-kier*, in which the goods, previously impregnated with dilute caustic soda, were submitted to the action of low-pressure steam.

The steamer-kier consists of a strong wrought-iron horizontal boiler, one end of which can be closed by a specially constructed sliding door. At the side of the kier stands a centrifugal pump connected with the top and bottom of the kier, and also with liquor tanks beneath, so that either boiling water or dilute caustic alkali solution can be sprinkled on and circulated through the goods. Figs. 6 and 7 show the general disposition of the steamer-kier.

Two waggons of cloth having been run into the kier, and the door closed, steam is admitted till the pressure reaches a maximum of 4–5 lbs. During the steaming or boiling process, a continual sprinkling of the cloth with dilute caustic soda (sp.gr. 1·01–1·02) is maintained, in order to keep the cloth well saturated with liquid, and thus prevent oxidation and consequent tendering of the fibre by the action of the steam. The excellent circulation of the liquors in the steamer-kier is a noteworthy and most important feature, since it greatly facilitates the saponification of the fatty matters on the cotton.

After steaming, the liquor is run off, the kier is almost filled with hot water, and this is circulated through the cloth by means of the centrifugal pump for one hour. A similar washing with fresh hot water takes place during another hour.

Each kier is provided with two pairs of waggons, so that while the goods in one pair are being steamed, the other pair can be emptied and refilled with cloth ready to be steamed. In this manner the operation of steaming is rendered as continuous as possible and a very great saving of time is effected.

The following details have been furnished by H. Koechlin, of the Loerrach Printworks:—

To effect the *madder bleach* by the *steamer-kier* process, the continuous bleach with the application of carbonic acid, &c., is omitted, the older method of chemicking and souring being preferred. Those who consider the lime-boil as essential may apply it equally well by means of the steamer-kier.

The operations in this case are as follows:—

1. *Lime-boil* (*or steam*). Run through milk of lime, 50 grams per litre, and pile in steamer-waggon; boil in steamer-kier 5 hours at 10 lbs. pressure, circulating 2000 litres water. Wash in kier with hot water.
2. *Sour.* Sour as usual with dilute HCl (sp.gr. 1·015); pile 2–3 hours, and wash.
3. *Ley prepare* Pass through NaOH solution (sp.gr 1·005-1·01), heated to 70° C, and pile in steamer-waggon.
4. *Ley-boil* (*or steam*). Boil 6 hours in steamer-kier at 10 lbs. pressure, with circulation of resin-soap liquor: 40 kilos. soda ash, 20 kilos. resin, 1000 litres water. Wash four times (½–1 hour each time) with boiling water, and finally with cold water, in kier.
5. *Chemicking.* Pass as usual through dilute bleaching-powder solution (sp gr. 1·0025); wash.
6. *Sour.* Pass as usual through dilute sulphuric acid (sp gr. 1·01); wash and dry.

Perfectly satisfactory results, however, are obtained by even *omitting* the lime-boil and proceeding as follows:—

1. *Sour.* Pass as usual through dilute H_2SO_4 (sp.gr. 1·015); pile 2–3 hours; wash and squeeze.
2. *Ley-prepare.* Pass through following solution at 70° C.: 20 litres bisulphite of soda (sp.gr. 1·3), 20 kilos. NaOH (solid 72 p.c.), 1800 litres water; pile in steamer-waggons.
3. *Ley-boil* (*or steam*). Boil in steamer-kier 6–8 hours at 10 lbs. pressure, with circulation of resin-soap liquor: 20 kilos. NaOH (solid 72 p.c.), 40 kilos. soda ash, 20 kilos. resin, 2000 litres water; wash 4 times (½–1 hour each time) with boiling water, and once with cold water in kier.
4. *Chemicking.* As above.
5. *Sour.* As above; wash and dry.

With the exception of the employment of the steamer-kier and the use of bisulphite of soda, this process is essentially the same as that employed for many years with success by Messrs. Guillaume Frères of St. Denis.

The preliminary souring process effects the decomposition of any insoluble fatty acid compounds present in the grey cloth; it removes calcareous or other mineral matter soluble in acids, and modifies any starchy matter present, probably rendering it more soluble. The addition of the small proportion of the reducing agent bisulphite of soda, along with the caustic soda in the preparing process, is intended to prevent any oxidation and consequent tendering of the cotton during the steaming process. The use of resin-soap along with the caustic soda, combined with the perfect circulation of the liquor, is very material to the success of this method of madder bleaching, for reasons already stated.

According to H. Koechlin, this method gives a perfectly satisfactory bleach. The white is not permanently stained in an alizarin dye-bath, and does not become yellow on steaming.

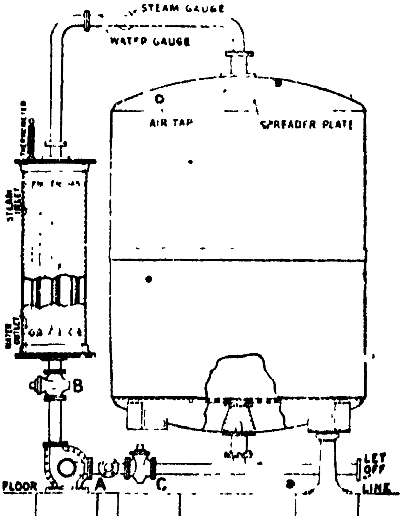


FIG. 8.

A noteworthy invention of Dr. G. Lunge is the application of acetic acid in connection with bleaching powder, in place of mineral acids or carbonic acid. It can be applied immediately before or after, or even along with, the solution of bleaching powder. It liberates hypochlorous acid with formation of soluble calcium acetate. When the hypochlorous acid exercises its bleaching power, it gives up oxygen and produces hydrochloric acid, which immediately acts upon the calcium acetate. In this manner the acetic acid is reproduced, and is thus ready to decompose fresh portions of calcium hypochlorite.

Hadfield and Sumner patented a process in which the cloth, after having been impregnated with a solution of bleaching powder, is passed through a box containing acetic acid vapour.

A solution of sulphurous acid has been used by some bleachers for the final souring process in place of sulphuric acid, over which it possesses the advantage of being an antichlor, in consequence of its reducing action.

The Walsh kier. In this kier, shown in Figs.

8 and 9, wh [illegible] gely used, the boiling liquor is circulated by means of a centrifugal pump, and it is heated in a special heating arrangement outside the boiling kier.

In the *Bentz-Edmeston* and in the *Tagliani-Rigamonti* kiers the boiling operation is a continuous process. Low pressure is usually employed, and the impregnation of the pieces with the boiling liquor in the lower part of the kiers is followed by steaming in the upper part. After the boiling is completed the pieces are plaited into wooden boxes, in which they are allowed to lie for some hours.

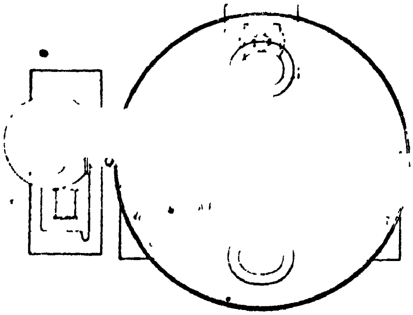


FIG. 9.

Piece goods, such as heavy twills, &c., which are frequently damaged (creased) in ordinary bleaching in the rope form, are treated in the open width. Special kiers have been constructed for this purpose, the principal one being the *Jackson-Hunt* kier (Fig. 10).

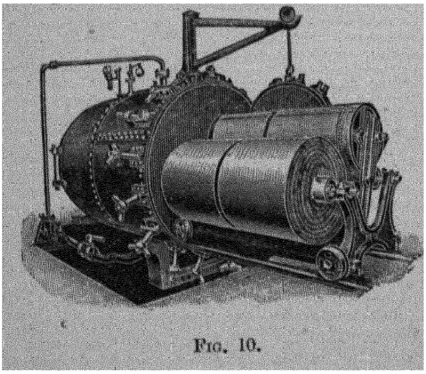


FIG. 10.

Previous to boiling in this kier the cloth is impregnated with caustic soda ley, which has been used in a former boiling, in a special [illegible] machine. In this the cloth travels [illegible] forated drum, and the soda ley is [illegible] ough it by means of steam, which is blown against it whilst it travels over the drum. Ultimately, the cloth is wound tightly and evenly into a batch.

This batch is now placed on a waggon, which is transferred to the horizontal boiling kier.

Special driving gear is provided, by means of which the cloth is wound off the batch on to another batching roller, passing over a heavy perforated drum which rests on both batches. The caustic soda liquor is circulated by means of a centrifugal pump, and is showered over the cloth during its passage over the perforated drum.

In this kier the cloth is usually boiled under high pressure (about 45 lbs.).

In the preparation of *sodium hypochlorite* solution, by electrolysing a solution of common salt two types of processes are employed, one in which the products of electrolysis, viz. sodium and chlorine, are not allowed to combine, and the other in which they are allowed to combine to form sodium hypochlorite

$$2NaOH + Cl_2 = NaOCl + NaCl + H_2O.$$

The latter process comes chiefly into consideration as regards the bleaching of textile materials.

The apparatus used may be divided into two classes, the one in which electrodes made of platinum-iridium are used, and the other in which carbon electrodes (highly compressed graphite) are employed.

In the Kellner electrolyser, which belongs to the former kind, a centrifugal pump is employed by means of which the salt solution is repeatedly passed through the apparatus until it contains from 3 to 5 grams of active chlorine per litre.

In the Haas and Oettel electrolyser, which belongs to the latter kind, the salt solution is electrolysed until it contains from 10 to 15 grams of active chlorine per litre.

Powerful circulation of the salt solution is obtained by means of the hydrogen gas evolved during electrolysing.

Bleaching by means of electrolytically prepared hypochlorite solution, although employed with advantage in special cases, such as the bleaching of cops, is not commonly practised, because it is more expensive in its application than bleaching powder.

The statement that an electrolytically prepared bleaching solution is more effective than a solution of bleaching powder containing the same amount of active chlorine, cannot be confirmed in practice.

Permanganate of potash, *sodium peroxide*, and *hydrogen peroxide* give excellent results in bleaching. Their price, as compared with bleaching powder, is, however, in most instances, prohibitive.

The history of cotton bleaching may be briefly said to comprise the following noteworthy improvements:—

1. The use of chlorine gas by Berthollet in 1787, and of hypochlorite of lime in 1799 by Tennant.
2. The boiling with carbonate of soda instead of caustic soda, after the lime-boil, introduced from America about 1837. A more effectual decomposition of the lime-soaps was thus obtained.
3. The adoption of the lime-sour, as proposed by A. Scheurer-Rott in 1837.
4. The use of resin-soap in the ley-boils about the same period.
5. The introduction of high-pressure boiling kiers about 1844.
6. The use of caustic alkali and resin-soap in conjunction with the steamer-kier, to the exclusion of the lime-boil, in 1883–84.

Linen bleaching. Since the retted flax fibre contains a much larger proportion of natural impurities than cotton, *e.g.* 25–30 p.c. of pectic acid, beside fatty matter, &c., linen is not so readily bleached as cotton. In the main, however, the methods adopted for the two fibres are the same. Linen is bleached in the form of yarn, thread, or cloth.

Linen-yarn bleaching. Very frequently linen yarn is only partially bleached, the process being completed, if necessary, when the yarn has been woven into cloth.

The following operations are employed in order to obtain 'half-white' or cream, with 1500 kilos. yarn, using low-pressure kiers:

1. *Ley-boil.* Boil 3–4 hours in a solution of 150 kilos. soda ash; wash and squeeze.
2. *Chemick* (*reel*). Reel 1 hour in bleaching-powder solution, sp.gr. 1·0025; wash.
3. *Sour.* Steep 1 hour in dilute sulphuric acid, sp.gr. 1·005; wash.
4. *Ley-boil* (*scald*). Boil 1 hour in a solution of 30–75 kilos. soda ash; wash.
5. *Chemick.* Reel in a dilute solution of bleaching powder, sp.gr. 1·0025; wash.
6. *Sour.* Steep 1 hour in dilute sulphuric acid, sp.gr. 1·005; wash well and dry.

If the yarn should be bleached more completely, then operations 4, 5, and 6 are repeated two or three times, as may be found necessary, with this difference, that between 4 and 5 the yarn is 'grassed,' *i.e.* exposed in the field to the action of the air, light, and moisture, for several days. By introducing this very gentle method of bleaching, the full strength of the fibre is better maintained.

The various operations are conducted in apparatus precisely similar to that employed in the bleaching of cotton yarn, except in the operation of chemicking. Although steeping under the sieve in dilute bleaching-powder solution might well be employed, it is usual to suspend the hanks of linen yarn on reels in such a manner that they are only partially immersed in the solution contained in a shallow tank. As the reels revolve the yarn becomes thus alternately impregnated with the solution and exposed to the air. The liberation of hypochlorous acid by the carbonic acid of the air is advantageous, and the bleach is more effective and regular.

The application of acetic acid, as proposed by Lunge, instead of this exposure to air, may here be strongly recommended, since then no insoluble lime salt is fixed on the fibre, and the subsequent souring is reduced to a minimum.

To avoid the presence of caustic lime, some bleachers use hypochlorite of magnesia, as proposed by Hodge, instead of bleaching powder.

Linen-cloth bleaching. The old method of bleaching linen cloth consisted in alternately boiling the fabric with solutions of sodium carbonate and exposing on the grass, succeeded by souring, and rubbing with solutions of soap. The modern method, adapted from that employed for calico, is given in the following *résumé*. It is intended for 1500 kilos. brown linen, using low-pressure kiers.—

1. *Lime-boil.* Boil 14 hours with 125 kilos. lime, 2000 litres water; wash.
2. *Sour.* Steep 2–6 hours in dilute hydrochloric acid, sp.gr. 1·0025; wash in stocks, *turn-hank*, wash.
3. *Ley-boils.* First, boil 8–10 hours with 2000 litres water containing resin-soap; 30 kilos. caustic soda (solid), 30 kilos. resin, previously boiled together with water; secondly, boil 6–7 hours with 2000 litres water, 15 kilos. caustic soda (solid), previously dissolved; wash.
4. *Expose in field* 2–7 days according to the weather.
5. *Chemick.* Steep 4–6 hours in dilute bleaching-powder solution, sp.gr. 1·0025; wash.
6. *Sour.* Steep 2–3 hours in dilute sulphuric acid, sp.gr. 1·005; wash.
7. *Ley-boil* (*scald*). Boil 4–5 hours, with 2000 litres water, 8–13 kilos. caustic soda (solid); wash.
8. *Expose in field* 2–4 days.
9. *Chemick.* Steep 3–5 hours in dilute bleaching-powder solution, sp.gr. 1·0013; wash.

At this stage the cloth is examined; those pieces which are sufficiently bleached are soured and washed, the rest are further treated as follows:—

10. *Rub* with rubbing boards and a solution of soft soap.
11. *Expose in field* 2–4 days.
12. *Chemick.* Steep 2–4 hours in dilute bleaching-powder solution, sp.gr. 1·0006; wash.
13. *Sour.* Steep 2–3 hours in dilute sulphuric acid, sp.gr. 1·005.
14. Wash, squeeze, and dry.

If the linen is not brown, but made of yarn already partly bleached, the above process is much curtailed, and weaker liquors are employed.

The kiers, chemicking and souring machines are the same as those used in cotton-cloth bleaching. The washing is done in the so-called wash-stocks or by slack-washing machines. The latter are very similar to the cotton-washing machines, the chief difference being that the water tank is divided into compartments, each of which holds a few yards of slack cloth forming each strand, before it passes through the squeezing rollers.

The 'rubbing' referred to is for the purpose of removing mechanically any remaining brown particles of ligneous matter termed 'sprits.' It consists in passing the chain of cloth through a solution of soap, and then immediately between a pair of horizontal, corrugated, heavy boards; the upper board rests loosely upon the lower one, and moves lengthwise to and fro, while the pieces pass between them at right angles.

The operation of 'turn-hanking' consists in disentangling the pieces after they have been washed in the stocks, and then refolding them for a further wash, thus ensuring a thorough cleansing of every portion of the cloth. When slack-washing machines are employed, the operation is of course not necessary.

The chemistry of linen bleaching is essentially the same as that of bleaching cotton. The pectic acid, fatty matters, &c., are rendered soluble by the alkaline boilings, and the colouring matters still remaining are oxidised and destroyed by hypochlorites. The repetition of these operations is considered necessary by reason of the large percentage of impurities present; but it is very probable that good results would be obtained by adopting the more rational plan of first removing the whole of the pectic and fatty matters before applying the hypochlorites.

A process of boiling linen goods preparatory to the bleaching has been patented by Cross and Parkes. The pieces are first impregnated with a solution of soap, silicate of soda, caustic soda, and mineral oil. They are then wound on a batching roller in a chamber containing steam, and afterwards steamed for some hours. This is followed by boiling with a solution of silicate of soda or of soda ash. The goods are finally washed; they are now ready for the first 'dip.'

Wool scouring and bleaching. The bleaching of wool never forms a separate industry, as in the case of cotton and linen, and, although in itself of minor importance, it is necessarily preceded by the operation of 'scouring,' which is of fundamental importance both to the woollen manufacturer and the dyer.

In its natural condition the wool fibre is contaminated with 15–80 p.c. of foreign matter, consisting partly of dirt, &c., derived from without, but mainly of certain fatty matters designated as 'yolk,' secreted by the animal from which it is derived. This secretion is separable into two parts—the one, 'wool-perspiration,' is soluble in water, and consists essentially of the potassium compounds of oleic and stearic acids (potash soaps), &c.; the other portion, termed 'wool-fat,' is insoluble in water, and is composed of cholesterol and iso-cholesterol, which exists partly in the free state, but chiefly in combination with oleic acid and other fatty acids.

Loose-wool scouring. The object of scouring wool is to remove from it the yolk, &c., and thus render it more suitable for spinning, dyeing, or bleaching. Two methods of effecting it may be employed. The one generally adopted is to treat the wool with dilute alkaline solutions capable of forming emulsions with the yolk; the other mode is to submit the wool to the successive action of fat solvents, carbon disulphide, &c., and of water.

Scouring with alkaline solutions. When carried out in the most complete manner, this method comprises the following operations:—

1. *Steep* several hours in tepid water.
2. *Scour* 15–30 minutes with dilute alkaline solutions (soap, sodium carbonate, &c.) at about 50° C.
3. *Wash* with water.

The *steeping* is performed in a series of large iron tanks, in which the wool is systematically washed or rather steeped in water heated to 45° C., until it is deprived of soluble matter. As a rule, two or three steeps with fresh water are found sufficient; but it is customary to pass the wash-water through several lots of wool until it becomes well saturated with 'wool-perspiration.' It is particularly advantageous in the case of wools rich in yolk (*e.g.* Buenos Ayres wool, &c.), since it prevents too rapid soiling of the scouring bath and consequent staining of the wool, and thus it tends to ensure more complete scouring. By evaporating the waste steeping liquors to dryness, and calcining the residue, a good quality of potassium carbonate, containing very little sodium salts and suitable for glass manufacturers, is obtained.

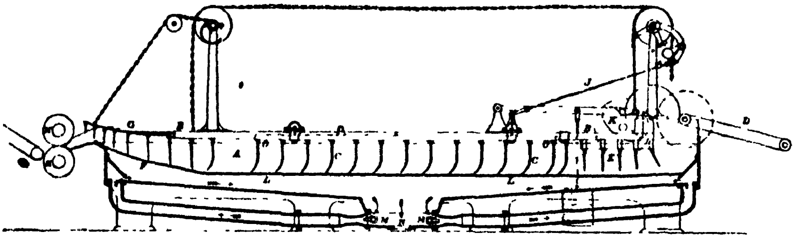


FIG. 11.

The *scouring and washing* of the wool in order to remove the remaining 'wool-fat' is best performed by the aid of so-called wool-scouring machines, one of which (J. & W. McNaught's) is shown in Fig. 11.

It consists of a large rectangular trough, A, with a light frame, B, suspended over it by chains and carrying a series of transverse, fixed, vertical rakes or combs, C.

The wool either in its raw condition or after steeping, is spread evenly on the moving endless apron or feeder D; it is thus continuously introduced at one end of the trough.

By suitable mechanism the frame is lowered, and the wool is at once pressed beneath the surface of the scouring liquor by the perforated tray or sieve E. When the frame is sufficiently lowered, it moves forward, the rakes gently carrying the wool towards the other end of the trough. When the forward stroke is completed, the frame is lifted up, the rakes rise vertically out of the liquid, and the frame returns to its original position. By these successive movements the wool is slowly passed through the scouring liquor. At the delivery end it is carried up the inclined plane F by the rakes fixed on the small frame G, which is hinged to the larger one. Having been pushed over the ridge, the wool slips down between the squeezing rollers H, H, ready to be passed through a second similar machine.

The working of the machine as above described, is suitable for Botany and other fine classes of wool. When washing low Cape, River Plate, and similar wools, which contain much dirt and sand, an additional movement is given to the rakes while in the liquor. This is effected by having the rakes fixed in a second frame, OO, which receives a slight backward-and-forward movement by means of the rod O and the cam K during the inward movement of the main frame BB, to which it is attached. By this means the wool is slightly opened out and agitated, and the sand and dirt fall through the perforated grating LL. When the scouring liquor becomes too soiled for further use, the steam injectors MM are brought into action in order to stir up all sediment, and the dirty liquor is run off by the plug-hole N.

For a complete arrangement there should be at least three such machines placed in line, so that the wool passes automatically from one to the other. The first contains more or less soiled scouring liquid which has been previously used in the second trough; the second contains fresh scouring liquid; and the third a continual flow of clean, cold, or preferably tepid water.

The choice of scouring agents depends upon the character and quality of the wool. For fine lustrous wools and such as are poor in yolk, a mild scouring agent should be selected, *e.g.* soap, ammonia, ammonium carbonate, 'lant,' &c., that is to say, agents which are capable of removing the yolk with the least injury to the fibre. The best soaps to use are those which are most soluble and least likely to contain any trace of caustic or carbonated potash or soda. Should these injurious constituents be present, the soap solution may be de-alkalised by the addition of a small quantity of boracic acid or ammonium chloride, thus yielding the less injurious alkali borates and ammonia, respectively.

Potash soaps, being very apt to contain excess of alkali, should be critically examined. An excellent and very soluble soap may be readily made from oleic acid and caustic soda.

Although a perfectly neutral soap does not always effect a rapid and complete removal of yolk, still it is better to adopt it, since one can always add the proper quantity of other agents, *e.g.* sodium carbonate, ammonia, &c., when necessary.

For low-class wools containing a large proportion of yolk, and when cheapness is a desideratum, sufficiently satisfactory results are obtained by the proper use of sodium carbonate free from caustic soda or other injurious impurity. Suitable sodium carbonates are sold under such commercial names as refined soda ash, Solvay soda, concentrated crystal soda (Brunner, Mond, & Co.), crystal carbonate (Gaskell, Deacon, & Co.), &c.

It is impossible to give precise data with respect to the concentration and temperature of the scouring solution to be employed, since these vary somewhat according to the character of the wool operated upon. If the best results are to be obtained, the solutions must always be applied as dilute and at as low a temperature (not above 50° C.) as is consistent with the complete removal of the yolk.

The waste scouring liquors are collected in large tanks and neutralised with sulphuric acid; the liberated fatty acids are sold to oil refiners, who by distillation obtain purer products, suitable for making soap.

Scouring with volatile liquids. This method is still only in an experimental stage. Mechanical difficulties, the fear of fire and explosions, the first cost of the scouring agent, &c., seem to have prevented the general adoption of this process. Its advantages are that the wool-fat is more completely removed than by the emulsion method, and the wool itself is not injured. A certain degree of success has been obtained by the method proposed by T. J. Mullings, and tried on a large scale. It consists in submitting the wool to the action of carbon disulphide in a closed centrifugal machine until the whole of the wool-fat is dissolved, then expelling the solvent by means of water, and not as heretofore by heat or steam, which always leaves the wool with a yellow colour. The wool must afterwards be washed in warm water to remove wool-perspiration and other impurities. The wool cleansed in this manner is said to be stronger, capable of spinning finer yarn and with less waste and at less cost than if scoured by the ordinary method with soap.

The same principle is adopted in the process of Singer & Judell of Adelaide, who employ, however, a more elaborate and more perfect apparatus, whereby the scouring is made continuous. The raw wool is placed on a feeding apron and carried along between two broad endless bands of wire gauze, first through a succession of fourteen tanks containing carbon disulphide and then through five containing water, all suitably enclosed. The wool, still held between the wire gauze bands, then passes between hot rollers in a steam-heated drying chamber and emerges in a scoured, washed, and dried condition. Arrangements for automatically collecting the dirt which settles from the carbon disulphide, for separating the latter from the water, distilling and returning it to the scouring tanks with the least possible loss, are all provided for by ingenious devices, and the general arrangement seems eminently typical of the method of scouring wool to be adopted in the future. It is said to have been worked with success in Australia.

Woollen-yarn scouring. The object of scouring woollen yarn is to remove the oil with which wool has been impregnated by the spinner. Precisely the same agents are used as for loose wool, but the machinery employed is necessarily different.

Those yarns which have a tendency to curl up because they have been highly twisted are submitted to the preliminary operation of 'stretching'; it also prevents them from shrinking during the subsequent scouring process.

The hanks of yarn are suspended on the arms of a strong iron frame and tightly stretched by means of screws. Thus charged, the frame is immersed in boiling water for a few minutes. After changing the position of the hanks on the arms, the operation is repeated, the yarn is allowed to cool in the stretched condition, and is then removed ready for scouring.

The scouring of yarn is effected either by hand or by machine. In the first case the hanks of yarn are suspended on wooden rods placed across a rectangular steam-heated tank containing the scouring liquor. During a period of 15 to 20 minutes the rods are swayed to and fro by hand, one by one, each hank being frequently turned in order to expose every por-

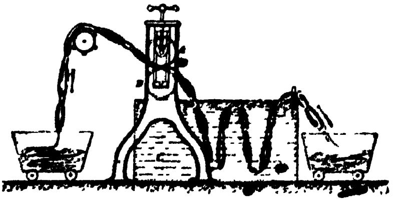


FIG. 12.

tion to the action of the liquor. The yarn is washed in another tank in the same manner.

Yarn-scouring machines are to be met with in several forms. A very effective one consists of a rectangular tank, C, having several rollers above and below, and a pair of squeezing rollers, A, B, situated at one end. The hanks of yarn, linked together by means of string loops, are passed continuously through the scouring liquor, and are then washed in a similar machine (*see* Fig. 12).

Woollen-cloth scouring. Woollen cloth is also scoured for the purpose of removing the oil with which the yarn is impregnated by the spinner. The operation consists in passing the cloth as an endless band, either in the strand form or in the open width, through the scouring liquor and then through a pair of squeezing rollers.

For thick woollen cloths, flannels, &c., scouring in the strand is preferred, since a certain amount of felting takes place and the cloth acquires a better handle. For worsted goods and such as are liable to crease, scouring in the open width is preferable.

Fig. 13 shows a section of E. Kempe's machine for this purpose. It consists of two squeezing rollers, A and B, placed above the wooden trough C containing the scouring liquor. The roller D serves to draw the cloth from the squeezing rollers, and causes it to fall in regular folds upon the inclined plane EE. This is covered with corrugated zinc, the grooves of which run longitudinally, in order to reduce the friction of the cloth, and to prevent the latter from moving to either side. The upper part of the inclined plane is hinged at F, so that the inclination of this part can be regulated to suit different qualities of cloth, and to ensure that it always slips down in regular folds without any tendency to fall over or become blocked. The perforated water-pipes G, G are for the purpose of washing the cloth after scouring.

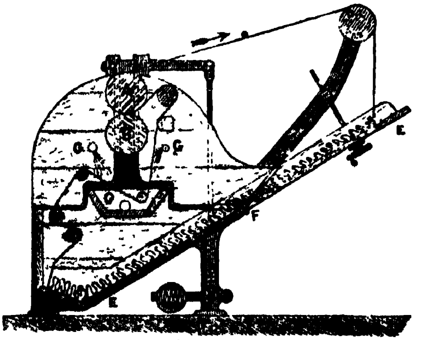


FIG. 13.

Bleaching of wool. After scouring, the wool still possesses a faint yellow tint, to remove which is the object of the bleaching proper. The agent almost universally employed is sulphur dioxide, either in the form of gas (gas-bleaching) or in solution (liquid bleaching). With hydrogen peroxide a more permanent white is obtained, but it is still too expensive to admit of extended application, but it serves as an excellent bleaching agent for certain fine materials.

Gas-bleaching, stoving, or sulphuring, consists in exposing the scoured and washed woollen material, while still wet, to the action of sulphur dioxide in a brick chamber. Yarn or thick cloth is suspended on poles, the sulphur (6–8 p.c. on the weight of wool) contained in an iron pot is ignited, the chamber door is closed, and the material is then left exposed to the action of the gas for six or eight hours, or even overnight. Thin cloth is generally passed in a continuous manner through a similar chamber provided with rollers above and below. The cloth in the open width enters through a narrow slit at one end of the chamber; it passes in a zigzag course under and over the rollers to the further end, then returns and passes out by the same slit. The sulphur dioxide is prepared in the stove itself, or it is produced in a separate furnace and led beneath the perforated floor of the chamber. According to the appearance of the fabric, it is passed through the bleaching chamber once or several times. Fig. 14 gives a sectional view of the sulphur stove for the continuous bleaching of cloth.

In **liquid-bleaching** the woollen material is immersed and moved about for several hours in a solution of sulphurous acid, or in one containing sodium bisulphite, and acidified with sulphuric acid. One may also steep the wool, first in a solution of sodium bisulphite and then in dilute sulphuric acid, and repeat the operations as often as may be necessary. The liquid-bleaching process has not met with that general acceptance to which it seems entitled.

After bleaching, the materials are well washed and tinted blue or bluish-violet, *e.g.* with refined indigo, indigo-extract, aniline-blue, methyl violet, &c., in order to counteract the yellowish tint which is so liable to return.

The bleaching action of sulphurous acid is most probably due to its reducing properties. According to this view, the sulphurous acid takes up oxygen from the water present, while the liberated hydrogen combines with the colouring matter of the wool to form a colourless leuco-compound. Another explanation, however, is that a colourless sulphurous acid compound is formed. Frequent washing of the wool with alkaline solutions restores the yellow colour. It seems evident, however, that the yellowing influence of alkalis is largely due to their further action upon the wool substance itself since they cause the wool eventually to become yellower than it was before bleaching.

Bleaching with hydrogen peroxide is effected by steeping the wool for several hours in more or less dilute solutions of this liquid, made slightly alkaline by the addition of ammonia. The simultaneous action of light accelerates and improves the bleaching. The white is very good and permanent, probably because, in this case, the colouring matter is destroyed by oxidation. Excessive bleaching by this method gives the wool a harsh feel. Lunge recommends a slight treatment with hydrogen peroxide of sulphur-bleached wool in order to oxidise and thus render innocuous traces of sulphurous acid not removed by washing. A very dilute solution of sodium hypochlorite and exposure to air will effect the same purpose.

Bleaching of wool with hydrosulphite of soda has been suggested by F. V. Kallab. It is prepared by adding zinc powder to a solution of bisulphite of soda. The zinc is precipitated by adding milk of lime.

Silk scouring and bleaching. The raw silk fibre consists essentially of two substances, *fibroïne* and *sericine*. The former constitutes the central portion of the fibre, and may be regarded as the fibre proper, while the latter resides principally in the external part and is readily removed by water and especially alkaline solutions.

Raw silk is harsh, stiff, lustreless, and more or less unsuitable for dyeing, but when the external sericine or silk-glue is removed it becomes soft and lustrous, and acquires an increased affinity for colouring matters.

The object then of scouring is to remove the silk-glue from the raw silk. It is effected by the two operations, '*stripping*' and '*boiling-off*.'

Stripping or ungumming. In order to remove calcareous or other mineral matter soluble in dilute acids, it is well first to rinse the silk in a tepid bath of dilute hydrochloric acid, and then wash. The hanks of silk are then hung on smooth wooden rods and worked, as in woollen-yarn scouring, in a soap-bath heated to about 90°–95° C. for about 20 minutes. A second and even a third bath may be used with advantage. Long working in one bath is not good, especially for silk intended to be white, since the silk (fibroïne) is apt to attract some of the colouring matter at first removed along with the silk-glue, and it is afterwards very difficult to remove. With yellow silk this point must be carefully attended to.

During the stripping operation the sericine at first swells up and makes the silk somewhat glutinous, but soon it dissolves off and leaves the fibre soft and lustrous. The waste soapy liquors, strongly impregnated with sericine, are carefully preserved and find an important use in silk-dyeing under the name of '*boiled-off liquor*.' When applying the coal-tar colours, it serves to retard their attraction by the silk, and thus ensures the production of even or level colours.

After stripping the silk is rinsed in water containing a small proportion of soap and sodium carbonate.

Boiling-off. The object of this operation is to complete the removal of the silk-glue and thus give the silk all the lustre and brilliancy of which it is capable. The hanks of silk are tied up in coarse bags of cotton or hemp, generally called 'pockets,' and these are boiled for one to three hours in open copper boilers. The silk is then well rinsed in a weak tepid solution of carbonate of soda, and finally in cold water.

During the operations above described, Japanese and Chinese silks lose 18–22 p.c. in weight, European silks lose 25–30 p.c.

Bleaching of silk. The actual bleaching of silk is effected by exposing the scoured silk, while still in the wet state, to the action of sulphur dioxide gas. The operation is precisely similar to the stoving of wool.

In certain cases, *e.g.* with so-called 'souple' silk, the stoving is preceded by a preliminary bleaching in *aqua regia*, diluted to sp.gr. 1·02 and heated to 20°–35° C. The silk is rinsed in this solution for 8–15 minutes until it acquires a greenish-grey colour, and then at once washed well in cold water. A dilute solution of the so-called 'chamber-crystals' of the sulphuric acid manufacture may replace the *aqua regia*.

The bleaching of silk with hydrogen peroxide is gradually being more and more adopted, especially for Tussur silk and other wild silks. Indeed, for these silks no other method of bleaching is so satisfactory. The silk is steeped and worked in a dilute solution of hydrogen peroxide, rendered slightly alkaline with ammonia or with silicate of soda or borax, until it is sufficiently bleached. A more rapid and effective method is to steep the silk in a somewhat stronger solution, then wring out the excess of liquid, and steam. The operations may be repeated until the silk is sufficiently bleached.

Tinting of silk. Bleached silk is finally tinted or dyed in delicate shades of blue, purplish-blue, cream colour, &c. For pure white it is usual to dye the silk in a very dilute solution of a suitable coal-tar colour. After tinting, the silk is slightly rinsed in water and dried in a moderately warm and darkened stove. J. Hü.

BLEACHING POWDER *v.* CHLORINE.

BLENAL. Carbonic acid ester of santalol

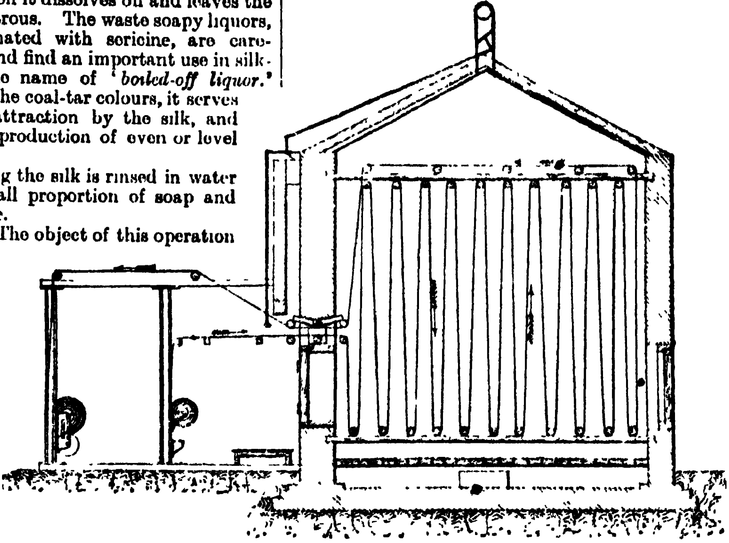


FIG. 14.

BLENDE, from *Blenden*, Ger., to dazzle. Native zinc sulphide. It usually contains iron sulphide which gives it a black colour, whence the name Black Jack applied to it. An important ore of zinc. The sulphur it contains is occasionally utilised in the manufacture of sulphuric acid. (For descriptions of burners for this purpose, *v.* J. Soc. Chem. Ind. 3, 631; 4, 54.) *V.* ZINC-BLENDE.

BLEU DIRECT or **DIPHENYLAMINE BLUE** *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLEU FLUORESCENT $C_{18}H_{6}Br_{4}N_{2}O_{5}(NH_{4})$. A colouring matter obtained by Weselsky and Benedikt in 1880 by treating diazoresorufin dissolved in potassium carbonate with bromine and precipitating by an acid. Soluble in boiling water with a red-violet colour, giving a fluorescent green solution. Dyes silk and wool blue with brownish fluorescence (Weselsky and Benedikt, Monatsh. 5, 605; Ber. 1885, 18; Ref. 76).

BLEU DE GARANCE. Artificial ultramarine (*v.* ULTRAMARINE; PIGMENTS).

BLEU LUMIÈRE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLEU DE LYON, BLEU DE NUIT, BLEU DE PARIS *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLEU MARIN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLEU DE SAXE *v.* COBALT.

BLEU SOLUBLE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLIND-COAL. A Scotch term for anthracite.

BLISTER STEEL *v.* IRON.

BLOCK FUEL *v.* FUEL; also PITCH.

BLOCK TIN *v.* TIN.

BLOEDITE. A hydrated double sulphate of magnesium and sodium, $Na_2Mg(SO_4)_2 \cdot 4H_2O$, forming water-clear monoclinic crystals, often of large size and beautifully developed. They are found in the salt mines of Stassfurt and in Austria, and in the Punjab Salt Range, India. Crystals 16½ cm. in length have been found in the black mud beneath a crust of sodium sulphate on Soda Lake, San Luis Obispo Co., California. Simonyite and astrakanite (from salt lakes near Astrakan) are synonyms.

L. J. S.

BLOMSTRANDINE. A rare-earth mineral consisting of a titano-columbate of yttrium-metals, thorium, uranium, &c., occurring as orthorhombic crystals in pegmatite veins at several localities in southern Norway. The large crystals of tabular habit are found in the felspar quarries, and those from the island of Hitterö are well known in collections. They are brown on the surface, but on a fresh conchoidal fracture the colour is black with a bright pitchy lustre. The mineral is optically isotropic, owing to alteration by hydration. Sp.gr. 4·82–4·93. These crystals were provisionally referred by W. C. Brogger in 1879 to æschynite (*q.v.*), an allied species differing mainly in containing cerium-metals in place of yttrium-metals. More recently, Brögger (Die Mineralien der südnorwegischen Granit-Pegmatitgänge, Videnskabs-Selskabets Skrifter, Kristiania, 1906) has given a detailed description of this material, and he gives several other Norwegian localities for the mineral, namely, near Arendal and in Sætersdal. He interprets the complex composition as an isomorphous mixture in varying proportions of a meta-columbate with a metatitanate; and for another member of the same series from the tin gravels of Swaziland, Transvaal, shown by G. T. Prior's analysis (1899) to contain more columbium with less titanium, he proposed the name priorite. These isomorphous minerals, blomstrandine and priorite, are respectively dimorphous with polycrase and euxenite; the four minerals euxenite-polycrase and priorite-blomstrandine thus forming an isodimorphous series.

The name blomstrandine is not to be confused with the earlier name *blomstrandite* (of G. Lindstrom, 1874), which was applied to an uncrystallised hydrated titano-columbate and tantalate of uranium with some calcium and iron, from a felspar quarry at Nohl, in Sweden (*v.* BETAFITE). L. J. S.

BLOOD is a richly albuminous fluid which holds in suspension large numbers of corpuscles. The fluid medium in which the corpuscles float is called the plasma, or *liquor sanguinis.* In round figures, the plasma contains about 10 p.c. of solids, of which proteins comprise 8, extractives 1, and inorganic salts (the principal one being sodium chloride) the remaining 1. The proteins are all coagulable by heat, and are named serum albumin, serum globulin, and fibrinogen. The last-named is the least abundant (0·4 p.c.), but confers upon the blood its characteristic power to clot or coagulate when it is shed. When shed, the blood rapidly becomes viscous, and then sets into a jelly; the jelly contracts and squeezes out of the clot a straw-coloured fluid called serum, in which the shrunken clot then floats. The formation of threads of a solid protein called fibrin from fibrinogen is the essential act in coagulation; this with the corpuscles it entangles constitutes the clot, and serum is plasma *minus* the fibrin which it yields. The following scheme shows the relationships of the constituents of the blood at a glance:—

$$\text{Blood}\begin{cases}\text{plasma}\begin{cases}\text{serum}\\ \text{fibrin}\end{cases}\\ \text{corpuscles}\end{cases}\left.\begin{matrix}\\ \\ \end{matrix}\right\}\text{clot.}$$

In round figures, the blood contains 60–65 p.c. of plasma, and 35–40 p.c. of corpuscles. The corpuscles are of three kinds, the red corpuscles or erythrocytes, the white or colourless corpuscles or leucocytes, and some very small particles also colourless, which are called the blood-platelets.

The subject of blood clotting has been the battlefield of numerous opposing theories, but the view now generally held is that the conversion of fibrinogen into fibrin is due to the action of an enzyme called thrombin or fibrin-ferment. This agent takes origin from the platelets and white corpuscles; it is first shed out from them in an inactive form called thrombogen; thrombogen is converted into the active enzyme thrombin by the combined action of the calcium salts of the plasma and of an activating agent termed thrombokinase, which originates from the cells of the blood itself and of the other tissues of the body.

The transformation of fibrinogen into fibrin has been regarded as a chemical change. But the recent work of Hekma (Biochem. Zeitsch. 1916, lxxiii. and lxxiv.) and of Howell (Amer. J. Physiol. 1916, 40) shows that the change is probably a physical one. Fibrinogen is the sol, and fibrin the gelphase of the protein. Fibrin is first deposited as ultramicroscopic particles (microns), then fine needle-like crystals appear; these by agglutinating together ultimately lead to the formation of typical fibrin threads.

The white or colourless corpuscles are typical nucleated animal cells which have been differentiated into varieties by their staining reactions, the number of their nuclei, and their seat of origin (lymphoid tissue, and red bone marrow). Their most important property is their power of amœboid movement, by which they ingest and subsequently digest foreign particles. They act in this way as scavengers (phagocytes), and thus confer protection against pathogenic organisms (bacteria, &c.).

The red corpuscles are much more numerous than the white, averaging in man 5,000,000 per cubic millimetre, or 400–500 red to each white corpuscle. It is these which give the red colour to the blood. They vary in size and structure in different groups of the vertebrates. In mammals they are biconcave (except in the camel tribe, where they are biconvex) non-nucleated discs, in man $\frac{1}{3200}$ inch in diameter; during fœtal life nucleated red corpuscles are, however, found. In birds, reptiles, amphibia, and fishes, they are biconvex oval discs with a nucleus; they are largest among the amphibians. Their most important and abundant constituent is the pigment hæmoglobin. In invertebrates this respiratory pigment is usually absent, and when present is, with few exceptions, in solution in the plasma and not in special corpuscles. In other invertebrates its place is taken by other respiratory pigments, for instance, by the green pigment which contains iron and is called chlorocruorin (in certain worms), or by the blue pigment which contains copper and is termed hæmocyanin (in certain crustaceans and molluscs). The vast majority of invertebrates have colourless blood containing only colourless corpuscles. Hæmoglobin contains 0·4 p.c. of iron; it and certain of its derivatives give characteristic absorption spectra which form one of the best tests for blood. It is termed a conjugated protein, consisting of a protein (globin) in combination with the iron containing material termed hæmatin

$$(C_{32}H_{30}N_4FeO_3)$$

Hæmoglobin is crystallisable, but hæmatin has not yet been obtained in crystalline form. By boiling dried blood with a little sodium chloride and glacial acetic acid, the characteristic brown crystals of hæmatin hydrochloride or hæmin are readily obtained, and this is the best chemical test for blood; it can be performed quite readily on a microscope slide. By treatment with acid, an iron-free derivative of hæmatin is obtained called hæmatoporphyrin, and in the body certain iron-free derivatives somewhat similar to hæmatoporphyrin are formed; these constitute the pigments of the bile. By the reduction of hæmatoporphyrin, hæmopyrrol (a mixture of pyrrol derivatives) is obtained, and the same substances are obtained also from phylloporphyrin, a derivative of chlorophyll; this is an interesting fact, as it indicates a near relationship between the principal pigments of the animal and vegetable worlds.

During life the blood is in constant movement (circulation), and it is owing to this circumstance that it supplies the tissues with both nutriment and oxygen. The products of protein and carbohydrate digestion pass directly from the alimentary canal into the blood-vessels; the fat reaches the blood indirectly by the lymph-stream. The blood, however, does not, except in the spleen, actually bathe the tissue elements; the middle-man between blood and tissues is a fluid called lymph, which exudes from the blood through the thin walls of the capillary blood-vessels. The lymph thus supplies the tissues with material for their repair or for storage; it also removes from the tissues the waste products of their activity; it is collected by lymphatic vessels, which converge to the main lymphatic channel called the thoracic duct. This opens into the large veins near to their entrance into the heart, and thus the lymph is returned to the blood, and the waste products are then conveyed to the various organs (lungs, kidneys, skin) by which they are discharged from the body.

The function of blood as an oxygen carrier is dependent on the presence of hæmoglobin. Oxygen passes by diffusion into the blood of the lungs, and is then seized by the pigment, with which it forms a loose compound called oxyhæmoglobin; this bright-red arterial or oxygenated blood passes to the heart, and is thence propelled by the arteries all over the body; in the tissues, where the oxygen tension is very low, oxyhæmoglobin is dissociated, and the oxygen passes into the plasma, and again reaches the actual tissue elements *viâ* the lymph. The reduction of oxyhæmoglobin changes the colour of the blood to the darker tint which it has in the veins, by which vessels it is carried back to the heart and sent to the lungs for a fresh supply of oxygen. The venous blood is also rich in carbonic acid, which finds an exit from the blood in the lungs into the expired air. It should be noted that hæmoglobin is not the exclusive carrier of carbon dioxide; the other proteins act similarly, but the gas is carried mainly as carbonates in the blood-plasma.

The amount of respiratory oxygen carried by the blood pigment is 1·34 c.c. oxygen per gram of hæmoglobin. This can be replaced by equivalent amounts of such gases as carbon monoxide or nitric oxide. These compounds are more stable than oxyhæmoglobin, and the gas is not removable by the tissues; hence in coal-gas poisoning the colour of the blood is equally bright in arteries and veins, and the cause of death is oxygen starvation.

The foregoing outline of the composition and uses of the blood from the physiological point of view can be amplified by the study of any standard textbook of physiology or physiological chemistry.

Passing now to the technical and commercial aspect of the case, the uses of the blood come mainly under four headings: (1) as food; (2) as manure; (3) as a clarifying agent; and (4) as a drug.

(1) As *food*. Blood as such is only used as food by savages, and attempts have been made to utilise dried defibrinated blood as a commercial food product without any great success. It, however, forms an important constituent of certain articles of diet, of which Black pudding and the German Blutwurst (Blood sausage) are

the best known. In the preparation of these pig's blood is most commonly employed, and they are of high nutritive value. (For the composition of various kinds of Blutwurst, *see* König, Chemie d. menschl. Nahrungs und Genussmittel, Berlin, 1904, 525; Pott. Handb. d. Tier-Ernahrung, iii. 513, 1909; E. Schmidt, Lehrb. d. pharm. Chem. ii. 2, 1833, 1901.)

(2) *As manure.* Dried blood, the so-called Blood-meal (Blutmehl), is extensively used as manure, and may be placed directly on the land, or, more frequently, is mixed with superphosphates. It is a brown powder with a glue-like smell, and must be kept in dry places to avoid putrefaction. It is valuable on account of its high percentage of nitrogen (11·8) and of phosphorus (1·2 p.c.). Numerous patent manures contain a certain proportion of blood. (For details, *see* König, *l.c.* 496; Merck's Waren-Lexicon, 5th ed. art. 'Blut.')

(3) *As a clarifying agent.* Blood is employed in the same way as milk, gelatin, and albumin are, as a clarifying agent for wines, syrups, and similar liquids, in the proportion of 150–200 c.c. of blood per litre. The clearing action is due to the proteins present, but used in this way there is considerable danger of infection, as also is the case for milk. Dried blood or the dried blood-albumin is therefore preferable. Blood-albumin is prepared from the serum drained off from the clot; the product is really dried serum, as the proteins are mixed with the other constituents of that fluid, and the word 'albumin' is used as synonymous with 'protein,' and not in the correct chemical sense. It has the advantage of being considerably cheaper than egg-albumin, for the total blood of an ox will yield 750–800 grams of the dried product, a good-sized calf will yield 340–400 grams, and a sheep about 200 grams (*see* Merck, *l.c.* art. 'Blutalbumin').

(4) *The therapeutic uses of blood and serum.* The high nutritive value of blood makes it a valuable drug in the treatment of anæmia, and certain patent medicines sold under the name of hæmatogen consist very largely of blood mixed with suitable flavouring and preservative agents. A still larger practical use of blood products (serum therapy) has been the outcome of work on immunity, in which the names of Richet, Ehrlich, Behring, and Roux may be mentioned as those of pioneers. Those interested in problems of immunity should consult current handbooks of pathology. The following does not pretend to do more than give a sketch of the main facts, and the example selected of the usefulness of the method is that in which serum therapy has been the most successful, namely, the treatment of diphtheria. The animal body is protected against its foes by a variety of mechanisms, and against our microscopic (bacterial) enemies the most potent of these is the action of colourless blood corpuscles (phagocytosis). This, however, is assisted in certain cases by the presence in the fluid part of the blood of chemical substances which have received a variety of names; for instance, 'bacteriolysins' are substances which actually kill bacteria; 'agglutinins' are substances which clump the bacteria together and render them immobile; 'opsonins' are substances which render bacteria an easy prey to leucocytes, either by adding something to them to make them tasty or removing something from them which makes them distasteful; and 'antitoxins' are substances which neutralise the poisons or toxins which are produced by the bacteria. There is very little accurate chemical knowledge of the composition of these various materials; they are, however, as a rule, destroyed by a high temperature, and are probably protein-like in nature. The amount of these substances in the blood may be increased by certain stimuli, much in the same way as the epidermis becomes thickened as the result of manual labour. The administration, for instance, of small doses of the toxin will produce an excessive production of the antitoxin which specifically neutralises the poison. Substances which in this way stimulate the production of these natural antidotes are spoken of in general terms as antigens.

If the bacilli which produce diphtheria are grown in a suitable medium, they produce the diphtheria toxin much in the same way as yeast will produce alcohol when grown in a solution of sugar. If a certain small dose of this poison is injected into an animal, it will produce death, and that is called the lethal dose. But if the animal receives a smaller dose, it will recover; a few days later it will stand a larger dose and recover more quickly; this is continued until after many successively increasing doses, it will finally withstand without ill effects an amount equal to many lethal doses. The animal is now immune against diphtheria, for the administration of the toxin (or antigen) has called forth an excessive production of antitoxin, and the blood remains rich in antitoxin for a considerable but variable time; the serum obtained from the blood of the immunised animal is then employed for injecting into other animals or human beings suffering from diphtheria, and rapidly cures the disease. The horse is the animal selected for the preparation of antitoxin, and the success of the new treatment in reducing the death-rate from what used to be considered a terrible disease is one of the wonders of modern medicine.

(5) *Miscellaneous uses of blood.* Blood is, or has been, employed in a number of industrial processes, but it will be sufficient here just to enumerate a few of them: thus it has been used as a medium for paints (Johnson, Eng. Pat. 82, 1883), in the preparation of adhesive cements, as a precipitant of sewage in the alum, blood, and clay process, and in the manufacture of pure animal charcoal.

Tests for blood. It is often necessary, in medico-legal practice, to be able to identify blood-stains on garments and instruments. If the blood is fresh, a microscopic investigation reveals the presence of corpuscles, and an aqueous extract will show the typical absorption bands of hæmoglobin with the spectroscope. The best chemical test is the formation of hæmin crystals already described, and is given by quite small quantities of blood, even if it is old and dry. When the blood is dry, and small quantities only are present, the most delicate spectroscopic test consists in dissolving it in dilute potash with the aid of heat, and then adding a drop of a reducing agent such as ammonium sulphide; the two absorption bands of reduced hæmatin are then seen, one about half-way between the D and E lines, and the other just on the blue side of the E line.

Human blood can only be distinguished with certainty from the blood of other animals by the so-called ‘biological reaction.’ The injection in successive doses of blood of another species into an animal acts as an antigen, and causes the development in the blood of the injected animal, of a specific ‘precipitin’; the addition of the blood to the serum of the animal which furnished the injected blood causes a precipitate; and such a precipitate does not form except between the blood of the two species of animal used in the experiment. This has been applied to the case of human blood, by taking a rabbit and injecting human blood into it. The serum of this rabbit will then give a precipitate with the blood of man (and to a less extent of the higher apes), and with the blood of no other species of animal. The test is extraordinarily delicate, and will detect human blood that has been dried for months, and even when it is mixed with the blood of other animals. W. D. H.

BLOODSTONE. A popular name for the mineral heliotrope, a variety of chalcedony (SiO_2), showing bright-red spots on a dark-green ground. It is much used for the engraving of ring-stones and seals.

The same name has also been used for hæmatite (Fe_2O_3), being a translation of *αἱματίτης*, so called because the colour of the powdered mineral is like that of dried blood.

L. J. S.

BLOOM. A term given to a mass of iron after it leaves the puddling furnace (*v.* IRON).

BLOOMERY. An old term for an iron furnace.

BLOWN OILS *v.* OILS and FATS.

BLOWPIPE *v.* ANALYSIS.

BLUBBER OILS *v.* OILS and FATS.

BLUE, ACETIN, *Coupier's blue* (*v.* INDULINES)

BLUE, ALIZARIN. This name is given to *dioxyanthraquinone-quinoline* $C_{17}H_9NO_4$, and its *sodium bisulphite compound*

$$C_{17}H_{11}NO_{10}S_2Na_2$$

(*v.* ALIZARIN AND ALLIED COLOURING MATTERS).

BLUE, ALKALI, NICHOLSON'S BLUE or **SOLUBLE BLUE** *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE, ANILINE. GENTIAN BLUE, OPAL BLUE, NIGHT BLUE, LIGHT BLUE, or **FINE BLUE** *v.* TRIPHENYLMETHANE COLOURING MATTERS; also ANILINE BLUE.

BLUE, ANTWERP, *v.* PIGMENTS.

BLUE, AZO-, *v.* AZO- COLOURING MATTERS.

BLUE, AZODIPHENYL, ACETIN BLUE, COUPIER'S BLUE, INDULIN, FAST BLUE R. $C_{18}H_{15}N_3Cl$ (*v.* INDULINES).

BLUE, BASLE. *Tolyldimethylaminophenotolyliminonaphthazonium chloride* $C_{32}H_{29}N_4Cl$ (*v.* AZINES AND COLOURING MATTERS DERIVED FROM THEM).

BLUE, BAVARIAN, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE, BENZIDINE, *v.* AZO- COLOURING MATTERS.

BLUE BLACK *v.* AZO- COLOURING MATTERS.

BLUE, BLACKLEY, *v.* INDULINES.

BLUE, BRILLIANT COTTON, METHYL BLUE, METHYL WATER BLUE. *Soda salt of triphenyl-β-rosanilinetrisulphonic acid* (*v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE, CERULEAN, *v.* PIGMENTS.

BLUE, CHINA, WATER BLUE 6 B EXTRA, OPAL BLUE, COTTON BLUE, MARINE BLUE, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE, CHINESE, or **PRUSSIAN BLUE** *v.* CYANIDES; also PIGMENTS.

BLUE, COBALT, *v.* COBALT; also PIGMENTS.

BLUE, COTTON, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE, COUPIER'S, *v.* INDULINES.

BLUE, CYANINE, *v.* PIGMENTS.

BLUE, DIPHENYLAMINE, BLEU DIRECT *Triphenyl-β-rosaniline hydrochloride* (*v.* TRIPHENYLMETHANE COLOURING MATTERS).

BLUE-ETHYLENE *v.* THIONINE COLOURING MATTERS.

BLUE, FAST, MELDOLA'S BLUE, NEW BLUE, NAPHTHYLENE BLUE. *Chloride of dimethylphenyl-ammonium-β-naphthoxazine* (*v.* OXAZINE COLOURING MATTERS).

BLUE, FLUORESCENT, *v.* BLEU FLUORESCENT.

BLUE, GENTIAN, SPIRIT BLUE O, OPAL BLUE, BLEU DE NUIT, BLEU LUMIÈRE, FINE BLUE, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE, INDIAN, *v.* PIGMENTS.

BLUE, INTENSE, *v.* PIGMENTS.

BLUE IRON-EARTH. An earthy blue variety of the mineral vivianite, a hydrated ferrous phosphate, $Fe_3P_2O_8,8H_2O$, often found as a blue powder encrusting vegetable remains and bones in bog-iron ore, peat, and clays. L. J. S.

BLUE, LEITCH'S, *v.* PIGMENTS.

BLUE, LIGHT, BLEU LUMIÈRE, LYONS BLUE, OPAL BLUE, BLEU DE NUIT *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE, METHYLDIPHENYLAMINE

$$C_{29}H_{24}N_3Cl$$

obtained in 1874 by Girard by the action of oxalic acid upon methyldiphenylamine. Or by the action of copper nitrate (Bardy and Dusart). Or with chloranil (Geigy). No longer made.

BLUE, METHYLENE, *v.* THIONINE COLOURING MATTERS.

BLUE, NEUTRAL, *v.* AZINES AND COLOURING MATTERS DERIVED FROM THEM.

BLUE, NILE, *v.* OXAZINE COLOURING MATTERS.

BLUE, PARIS, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

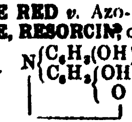
BLUE, PRUSSIAN, *v.* CYANIDES; also PIGMENTS.

BLUE, QUINOLINE, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BLUE RED *v.* AZO- COLOURING MATTERS.

BLUE, RESORCIN, or LACMOID $C_{12}H_9NO_4$?

probably



$$N\begin{cases}C_6H_3(OH)_2\\C_6H_3\begin{cases}OH\\O\end{cases}\end{cases}$$

, a colouring matter obtained by Weselsky and Benedikt in 1880, by the action of sodium nitrite on resorcin. Blue violet powder soluble in water. Soluble in alcohol with blue colour and dark-green fluorescence. Used as an indicator in alkalimetry (*q.v.*).

BLUE, SAXON, *v.* Cobalt.

BLUE, VICTORIA, *v.* Triphenylmethane colouring matters.

BLUE COPPERAS, BLUE STONE, or **BLUE VITRIOL.** *Copper sulphate* (*v.* Copper).

BLUE GUM TREE. The *Eucalyptus globulus* (Labdll.), a tree common in Tasmania and South-Eastern Australia.

BLUE JOHN. A variety of fluor-spar found in Derbyshire, and valued for making ornamental articles (*v.* Calcium).

BLUE LEAD. A term applied to galena by miners to distinguish it from white-lead ore, or carbonate.

BLUE PIGMENTS *v.* Pigments.

BOBBINITE *v.* Explosives.

BODY VARNISH *v.* Varnish.

BOFFINITE. An explosive consisting of potassium nitrate, 62–65 pts.; charcoal, 17–19½ pts.; sulphur, 1½–2½ pts., copper sulphate and ammonium sulphate, 13–17 pts.

BOG-BUTTER or **BUTYRELLITE.** A substance resembling adipocere (*q.v.*), occasionally found in peat in Ireland and elsewhere. (For list of chemical and physical constants of a sample of bog-butter found in Tyrone, *v.* Radcliffe and Maddocks, J. Soc. Chem. Ind. 1907, 3.)

BOGHEAD COAL *v.* Paraffin.

BOGHEAD NAPHTHA *v.* Paraffin.

BOG-IRON-ORE. An impure iron hydroxide of recent formation in bogs and marshes. It is referable to the mineral species limonite ($2Fe_2O_3, 3H_2O$), and, in fact, this name (from λειμών, a meadow) was at first applied to this material, which is known in German as Raseneisenstein or Wiesenerz (meadow-ore). It is sometimes placed under the species limnite (from λίμνη, a marsh), to which the formula $Fe_2O_3,3H_2O$ is assigned. It contains 20–78 p.c. Fe_2O_3, some silica and organic matter, and often phosphates in considerable amount. The material has been deposited by the oxidation, through the agency of algæ and bacteria, of chalybeate waters. It is dug in shallow pits in the peat bogs of Ireland, the production amounting to a few thousand tons per annum, and is mainly used for the purification of coal-gas. The Swedish lake ores (sjömalm) are of the same nature L. J. S.

BOG MANGANESE, *wad*, or earthy manganese (*v.* Manganese and Wad).

BOHEMIAN BOLE. A yellow variety of bole (*q.v.*).

BOILED OIL. Linseed oil (*v.* Linseed oil).

BOILER INCRUSTATIONS AND DEPOSITS. The deposition of insoluble salts directly through boiling the water in boilers, or through concentration beyond the limit of solubility of salts in solution, or again, by interaction between otherwise soluble salts leading to the precipitation of insoluble salts, causes serious trouble in boiler practice, and lowers the efficiency of the boilers. Any incrustation or scale retards heat transmission to the water, thereby increasing fuel consumption; overheating of the plates or tubes may result in serious damage, and the removal of a hard scale by mechanical means leads to further damage, in addition to the cost of removal and the boiler being idle for some time. If the deposit remains as a soft mud, frequent use of the blow-off cock is demanded, and heat is lost in the hot water blown off; but this, of course, is preferable to the accumulation of the deposit, and its baking on the plates or tubes to a hard mass.

The question of corrosion is also closely associated in many cases with the production of deposits, and treatment on scientific lines for the removal of the latter overcomes troubles from the former.

Natural waters vary widely in composition, and some are wholly unsuited for boiler use, either by reason of the formation of deposits and scale, or of their corrosive action. For the different characters of natural waters and their composition, *see* article on Water.

It is convenient to regard deposits as the soft material which can be removed as sludge; incrustations as deposits more or less firmly adherent to the boiler; and scale as the firm hard material which can only be removed with difficulty, usually requiring chipping off. Naturally no hard-and-fast line can be drawn between these forms.

Either form is to be associated primarily with the 'hardness' of water. 'Temporary hardness,' *i.e.* hardness removable by simple boiling, is due to calcium and magnesium carbonates (to a small extent also to ferrous carbonate). These salts, although almost insoluble in pure water, dissolve in the presence of carbon dioxide, owing to the formation of soluble bicarbonates ($CaCO_3 \cdot H_2CO_3$; $MgCO_3 \cdot H_2CO_3$). One litre of water holds about 1·2 grams of calcium carbonate (as bicarbonate) in solution; after prolonged boiling about 18–20 milligrams per litre. In the presence of other soluble salts the solubility is increased, thus with calcium sulphate present the solubility may be increased to 1·8 grams of $CaCO_3$ (as bicarbonate) per litre.

When water containing calcium bicarbonate is heated to about 65° C. it begins to deposit the normal carbonate in powdery form; at a later stage the deposit becomes crystalline, and may form a fairly adherent incrustation. Calcium carbonate exists in two crystalline forms, *calcite* (rhombohedral, belonging to the hexagonal system), and *aragonite* (orthorhombic, belonging to the rhombic system). The latter is harder and denser than calcite, and is believed by some authorities to be the cause of incrustation from carbonated waters. On boiling such waters the precipitate is a mixture of calcite and aragonite; the presence of other soluble salts favours the formation of aragonite.

Magnesium carbonate behaves somewhat differently, several intermediate hydroxy-carbonates being formed, the composition of which is dependent on temperature. By continued boiling in the presence of water at high temperatures (under pressure) magnesium carbonate forms the hydroxide ($Mg(HO)_2$), with liberation of carbon dioxide, and, according to J. H. Paul, insoluble magnesium oxide may even result. W. A. Davis (J. Soc. Chem. Ind. 1906, 788) found that on heating an alkaline solution of magnesium bicarbonate to 50° in a partially closed flask, the precipitate was $MgCO_3 \cdot 3H_2O$. At 100° it lost water ($2H_2O$), and at 125° the third molecule, together with carbon dioxide.

A table of solubility of magnesium carbonate in water containing carbon dioxide at various pressures will be found under Magnesium carbonate.

Solutions of magnesium carbonate decompose much more slowly on boiling than those of calcium bicarbonate, but the precipitation is more complete. In peaty waters the deposition of both carbonates is considerably retarded and may be prevented.

Ferrous carbonate behaves similarly to calcium carbonate.

The 'permanent hardness' is due chiefly to the sulphates of calcium and magnesium; to a minor extent to the chlorides and nitrates of these metals. Boiling at ordinary pressure does not cause the deposition of any of these salts, providing the water does not become too concentrated. On the other hand, boiling at the higher pressures existing in boilers almost complete precipitation of calcium sulphate occurs, and this constitutes the most troublesome constituent in boiler waters, being very largely responsible for the formation of hard adherent scales.

Calcium sulphate ($CaSO_4$) is practically insoluble in water. It occurs naturally in the hydrated form ($CaSO_4 \cdot 2H_2O$) as *gypsum*. Two varieties of the anhydrous sulphate are recognised; insoluble and soluble *anhydrite*. The solubility of natural gypsum attains a maximum at 32° C., 100 parts of water dissolving 0·2096 part. At 10° C. the solubility is 0·1929; at 100°, 0·1620 (Hulett and Allen, J. Amer. Chem. Soc. 1902, 24, 667). Much stress has been laid on the decreasing solubility with rise of temperature as the important factor in causing deposition in practice, but since the amount of calcium sulphate is generally much below the limit of solubility at 100°, it seems impossible that it can be an important factor. According to Silchester, at low boiler pressure (28–29 lbs.) water containing the salt will concentrate like other waters without scale, but at higher pressures (40–50 lbs.) will deposit, due to the formation of a hemihydrate, $2CaSO_4 \cdot H_2O$, at a temperature of 107°. This has been recognised by Johnston in scale from boilers working at 2 atmos. Above 130° the anhydrous calcium sulphate is formed. These are salient facts in the formation of hard scales due to this salt, for it is evident that it is not a question of concentration above the limit of solubility of $CaSO_4 \cdot 2H_2O$, but the definite formation of another phase, and the material being practically insoluble in this phase is almost completely precipitated even when present in very small amount in the water. 130°, or perhaps a little lower, may be regarded as the critical point determining the precipitation of calcium sulphate.

The solubility is increased by the presence of other more soluble salts such as sodium chloride and sulphate, and calcium sulphate may concentrate to a fairly high degree in a boiler water, as is shown by the following analysis by J. C. W. Greth:—

	Grains per Imperial gallon
Volatile and organic matter .	5·04
Silica	0·66
Calcium carbonate . .	1·20
Calcium sulphate . .	94·56
Magnesium sulphate . .	7·63
Sodium chloride . . .	12·66
Sodium sulphate . .	23·77

Other constituents of natural waters, such as calcium chloride, magnesium sulphate and chloride, often play an important part in the formation of scale by interaction; thus magnesium sulphate, although so soluble that it should never form part of a scale under proper working conditions, may be almost as troublesome as calcium sulphate, since with calcium carbonate or chloride it reacts with the formation of calcium sulphate and magnesium carbonate or chloride.

Formation of scale.—Waters which are in the main temporarily hard will deposit the carbonates of calcium and magnesium (also ferrous carbonate, if present), either in the boiler or feed-water heaters by the simple dissolution of the bicarbonates. Such deposits are usually powdery; in the presence of organic matter they seldom form coherent deposits, and so may be got rid of by the sludge cock. Under some conditions, however, the deposits bake on the plates or tubes and form incrustations. Further, on concentration of the water other salts in solution, like magnesium or sodium sulphate, may react on the incrustation with the formation of calcium sulphate and produce a much harder deposit—a true scale. Similarly, an incrustation containing magnesium hydroxide may react with magnesium chloride and form a hard incrustation.

The deposition of the carbonates is a gradual process so that a temporarily hard water which deposits much of its calcium carbonate in the feed-water heaters, but less of the magnesium carbonate because of its slower rate of deposition on heating, will continue to deposit in pipes, and such deposit will, for the same reason, contain a higher proportion of magnesium carbonate. Such actions are modified by the presence of other salts; thus, according to Petit, sodium chloride reduces the proportion of lime and increases that of magnesium, whilst magnesium sulphate causes more lime to be retained in solution.

Calcium sulphate, whether present as such or formed by interactions on concentration of the water, becomes deposited in the anhydrous form as soon as the temperature is above that corresponding to the phases $CaSO_4 \cdot 2H_2O$ or $CaSO_4 \cdot H_2O$. It forms an extremely hard scale of itself. If deposited amongst the precipitated carbonates it acts as a binder, and may form hard incrustations or scales. Its deleterious action may, therefore, be far greater than the mere proportion present would indicate. Calcium sulphate is throughout the most important factor in the formation of hard incrustations and true scales.

In broad terms, whilst the carbonated waters (temporarily hard) form soft easily removed deposits or incrustations, and waters containing calcium sulphate, or salts liable to form it by interaction (permanently hard), produce hard scales, and serve to bind loose incrustations into harder masses, such a generalisation must only be accepted as broadly true, for exceptions are not infrequent under the varying composition of natural waters and conditions of practice.

Magnesium hydroxide ($Mg(HO)_2$) with magnesium chloride forms a hard material; certain covering compositions for ships' decks are made on this basis. In the presence of calcium sulphate these salts form very hard porcelain-like scales, which are extremely difficult to remove. According to J. H. Paul, the tidal waters of the Thames give such a scale, the composition being very constant between 85–87 p.c. calcium sulphate, and 10–13 p.c. magnesium hydroxide, which approximately agrees with a molecular composition $3CaSO_4 \cdot Mg(HO)_2$.

Under bad conditions of working the concentration of the water in a boiler is sometimes allowed to increase to such an extent that soluble salts are deposited along with the true incrustation-forming solids. Paul gives the composition of such a scale from a feed-water containing 20 grains of lime and magnesia, and 40 grains of sodium salts per gallon as:—

Calcium carbonate . .	3·89 p.c.
Magnesium carbonate . .	1·16 ,,
Silica	0·69 ,,
Iron oxide	0·77 ,,
Sodium chloride . . .	77·09 ,,
Sodium sulphate . . .	11·82 ,,
Sodium carbonate . .	3·62 ,,
Combined water . . .	5·96 ,,

Ninety-five p.c. of this hard tough crystalline scale was soluble in water. The removal of scales of this 'soluble' type is simple, it being only necessary to blow down the boiler and fill up with fresh water and again empty.

The formation of scale from sea water is a matter of some importance, for although the use of sea water in boilers has been almost entirely discarded in favour of the use of distilled water for the 'make up,' made in the ship's evaporating plant, yet sea water frequently finds its way into the feed from leaky condensers, or through priming in the evaporator. The scale from sea water is mainly calcium sulphate, together with magnesium hydroxide and silica. Frequently the scale can be separated into a hard and soft portion, the latter containing a considerably higher proportion of magnesium hydroxide. The calcium sulphate may be between 80–90 p.c., magnesium hydroxide 2–5 p.c., calcium carbonate is usually under 1 p.c. One ton of sea water contains about 3·5 lbs. of scale forming salts, of which a little over 3 lbs. is calcium sulphate.

With low-pressure boilers it was possible to evaporate sea water without any serious trouble, providing the density was not allowed to become excessive (according to Lewes, to a density of 1·09 without deposition of calcium sulphate), but with modern boilers working at high pressures, so that the boiling-point was raised above the critical temperature of deposition of calcium sulphate in brine solution, troubles from scaling became so developed that the use of such water in these boilers had to be abandoned.

The formation of magnesium hydroxide is probably due to the interaction of the concentrated solution of magnesium chloride on the small amount of calcium carbonate which would be the first substance to deposit, the magnesium carbonate formed later losing carbon dioxide. Such a reaction accounts for the very small quantity of calcium carbonate in the scale. Magnesium hydroxide may also partly result by direct hydrolysis of magnesium chloride which takes place readily in contact with heated iron. Hydrochloric acid is set free, and this is closely associated with corrosion of the boiler on which it acts with the production of ferrous chloride, this further reacts with magnesium hydroxide in the absence of air. Free hydrochloric acid and iron are thus not found in the water; indeed the water is slightly alkaline, due to the solubility of the excess of magnesium hydroxide.

PREVENTION OF SCALE.

The treatment of water to prevent the formation of incrustations or scale may either be preparatory to its use in the boiler, or chemicals (generally sold as 'boiler fluids') may be added from time to time to the water in the boiler. In the latter case prevention of troublesome scale may be possible, the added fluids causing precipitation in a form which can be easily removed by the sludge cock, but unless all scale-forming materials can be kept in solution, an almost unrealisable condition, it is clearly more satisfactory to remove the causes of trouble before the water enters the boiler.

There is no relationship between the amount of impurity in a water and its scale forming character, since concentration will soon increase the quantity from even a very pure water. The essential point is the character of the dissolved solids, and accurate analysis is essential both from the point of view of determining suitability for boiler use, and the correct system of treatment necessary to render a natural water suitable.

With purely carbonated waters treatment in a special form of heater, whereby the calcium and magnesium carbonates are to a considerable extent precipitated, may be satisfactory, but in general chemical processes are employed. Although a large number of reagents have been proposed and adopted with success in special cases, three only find extended use, namely, lime (as milk of lime or as clear lime-water), sodium carbonate (soda ash), and sodium hydroxide (caustic soda). The action of lime on the bicarbonates is

$$CaCO_3 \cdot H_2CO_3 + Ca(HO)_2 = 2CaCO_3 + 2H_2O$$

$$MgCO_3 \cdot H_2CO_3 + Ca(HO)_2 = CaCO_3 + MgCO_3 + 2H_2O$$

The removal of calcium carbonate is never quite complete, and the reaction is still less complete with magnesium bicarbonate.

It can be ascertained when lime has been added in the requisite slight excess by the yellowish brown colouration the water gives with silver nitrate solution.

Lime has no action on the salts which cause permanent hardness, so that it is seldom employed alone, but generally in conjunction with soda ash or caustic soda. Either or both of these reagents may be employed without lime, and will remove both temporary and permanent hardness under suitable conditions. Soda ash reacts as follows:—

$$CaCO_3 \cdot H_2CO_3 + Na_2CO_3 = CaCO_3 + 2NaHCO_3$$

At temperatures above 160° the sodium bicarbonate is converted into the normal carbonate again, and carbon dioxide is liberated.

With caustic soda the reaction is similar, so that theoretically a small amount of either reagent is capable of dealing with the temporary hardness of a large quantity of water, but there is always the liability of the water becoming unduly alkaline by concentration.

With magnesium bicarbonate it is frequently found that when the correct quantity of is no precipitation in the cold. W. A. Davis (*l.c.*) states that this is due to the formation of the soluble salts

$$MgHCO_3{\cdot}CO_3.Na \text{ or } Mg(CO_3{\cdot}Na)_2,$$

according to the proportions used. Precipitation only occurs when the liquid is heated sufficiently to decompose these soluble double salts when a mixture of magnesium hydroxide and a basic carbonate, $Mg(OH){\cdot}(HCO_3)$, is precipitated. Consequently below a certain temperature it is impossible to completely soften magnesian waters containing small quantities of the bicarbonate, sulphate or chloride by means of either sodium carbonate or hydroxide.

It follows that a water containing magnesium salts if treated by these chemicals in the cold will deposit sludge or form an incrustation in a boiler or in feed-water heaters.

The action of sodium carbonate on calcium or magnesium sulphate causes precipitation of the respective carbonates and the formation of sodium sulphate. Sodium hydroxide forms calcium hydroxide and sodium sulphate, and the calcium hydroxide may then react on the salts causing temporary hardness, if these latter have not already been acted on directly according to the equation

$$CaCO_3{\cdot}H_2CO_3+2NaOH$$
$$=CaCO_3+Na_2CO_3+2H_2O$$

With these soluble alkalis it is important to note that the water will be left with free alkali in solution if the salts causing temporary hardness are in excess of the molecular equivalent of those causing permanent hardness. With calcium sulphate, on the other hand, in excess, or in molecular proportion, the sodium will all remain as sulphate

$$CaCO_3{\cdot}H_2CO_3+Na_2CO_3=CaCO_3+2NaHCO_3$$

(Mol. Wt. 100).

Above 160° C. $2NaHCO_3=Na_2CO_3+H_2O+CO_2$

$$CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4$$

(Mol. Wt. 136).

Accumulation of free alkali in boiler waters is objectionable ; it is commonly associated with priming or foaming, and if the solution be at all concentrated, may cause attack of brass boiler fittings and even of the gauge glass. For certain industrial purposes also alkaline water is inadmissible ; for example, in affecting delicate shades of colour in dyeing, and in the preparation of tan liquors.

Caustic soda requires using with discretion. It finds most useful application with waters containing the sulphates, chlorides and nitrates of calcium and magnesium.

Other chemicals which have been employed include magnesium oxide (or hydroxide), barium hydroxide and chloride, and the oxalates of potassium and sodium, but as they offer little advantage over lime and soda, and are very much more expensive, they are but seldom employed. Aluminium sulphate, alum solution, or sodium aluminate are sometimes employed.

A most successful system, both for boiler and industrial purposes, is the *Permutite* process, and this gives an almost perfectly softened water, and the process is one requiring the minimum of plant, it being simply necessary to pass the water through vessels containing the material. This is an artificial zeolite made by fusing together silica, alumina (or China clay) and sodium carbonate, and extracting the soluble portion with water. The crystalline product is a double silicate of alumina and soda, approximating to the composition $Al_2O_3{\cdot}Na_2O{\cdot}4SiO_2{\cdot}5H_2O$. Generally a portion of the soda is replaced by a small quantity of potash (K_2O) and lime.

Water is passed through the crystalline material when the sodium is replaced quantitatively by other metals, such as lime

$$Al_2O_3{\cdot}Na_2O{\cdot}4SiO_2+CaCO_3{\cdot}H_2CO_3$$
$$=Al_2O_3{\cdot}CaO{\cdot}4SiO_2+2NaHCO_3$$
$$Al_2O_3{\cdot}Na_2O.4SiO_2+CaSO_4$$
$$=Al_2O_3{\cdot}CaO{\cdot}4SiO_2+Na_2SO_4$$

The permutite may be regenerated when exhausted by passing strong brine through it, and this therefore is practically the only softening agent consumed.

With the ordinary permutite waters containing iron cannot be treated, and a special form containing a proportion of the higher oxides of manganese is used. This causes oxidation of ferrous to ferric salts, which are precipitated.

According to Bahrdt the reactions between the alkaline earth metals and permutite are reversible, and calcium can displace magnesium from magnesium permutite if first formed, and more magnesium may at times be present in the treated than in the untreated water. Bahrdt therefore recommends prior removal of the temporary hardness by lime and confining the permutite treatment to the removal of permanent hardness. Such treatment would require to be carefully controlled, as a too highly alkaline water spoils permutite.

The point must be emphasised that whilst with lime in the correct proportion to remove temporary hardness the precipitate is wholly insoluble, and no soluble salts are formed, with practically all other reagents an insoluble and soluble salts are formed. The latter will increase by concentration in the boiler, and care must be taken that this does not become excessive. Especially is this important where the soluble salt is alkaline.

Softening plant. Numerous forms of plant are employed for carrying out the softening process ; in some the sludge is allowed to settle, two tanks being used alternately. To decrease the settling period the sludge is generally stirred up with the fresh charge, and since the upper portion of the water clarifies first considerable saving of time (and consequent reduction in size of tanks) is possible by the use of a draw-off pipe carried by a float. Many softening plants are provided with automatic means of measuring in the required reagents in the proportion determined by analysis, also with mechanically operated stirrers and suitable filtering arrangements. It has been found that the softening process is more complete when there is an accumulation of precipitated material in the filters, which suggests that the action of the sludge left in settling tanks is beneficial beyond its mere mechanical action in promoting clarification.

With waters softened by the lime-soda treatment, even with heat, the reactions are often not completed in the tanks, and deposits are found in the feed-water heaters and pipes. These incompleted reactions are primarily due to magnesium salts, the behaviour of which has already been referred to. In the Archbutt-

Deely process this trouble is overcome by passing carbon dioxide into the softened water, the gas being drawn off from a coke fire, freed from sulphur dioxide by limestone, and injected by the steam blower, which serves to draw the gases from the small producer.

Boiler Fluids.

The use of an anti-incrustation fluid in the boiler is greatly favoured by many engineers, but is not such a satisfactory method of treatment as the prior removal of the scale-forming constituents. The method has the advantage of requiring no external plant, and for one or two boilers this is an advantage; but for larger installations a proper softening plant is better and more general in practice. It is obvious that precipitation of any solids by the boiler fluid takes place in the boiler, and the sludge so formed must be blown out at intervals. Some of the compounds used are not without action on boiler plates, tubes and fittings, especially copper alloys.

Sodium carbonate and hydroxide with waters containing little of the bicarbonates of lime and magnesium, especially if the water is slightly acid, give good results. With carbonated waters the alkali will not be used up and the water may become objectionably alkaline.

Ammonium chloride reacts with calcium carbonate, producing calcium chloride and ammonium carbonate, and the latter is decomposed at boiler temperatures, ammonia escaping in the steam. With magnesium salts magnesium chloride may be formed, and this is an active corrosive agent.

Sodium phosphate ($Na_2HPO_4 \cdot 12H_2O$) is suitable for sulphated waters. Bicarbonates are also decomposed, apparently through hydrolysis of the salt in solution with the formation of a small amount of sodium hydroxide.

Sodium sulphite and silicate are also sometimes employed. The former precipitates calcium sulphite, which is slowly oxidised to sulphate, in a non-crystalline form so that it can be blown off. Sulphites are, however, likely to cause corrosion, especially in the presence of nitrates, which become reduced to nitrites, and as these decompose active corrosion may result. The objection to sodium silicate is its liability to harden otherwise soft incrustations.

Many organic substances of the most varied character, starchy, albuminous and gelatinous materials, are used. The general action appears to be due to their colloidal character, which prevents the formation of crystalline deposits.

Tannic acid, or sodium tannate, have been widely employed. The free acid decomposes the carbonates with the formation of insoluble tannates. Tannic acid may act on the iron, and should only be used with alkaline waters, and then under careful chemical supervision. Alkaline solutions containing more or less sodium tannate are frequently employed, but it is probable that the anti-incrustation action is mainly physical and due more to the organic extractives than the sodium tannate itself, except in so far as the alkali itself acts in accordance with reactions already dealt with.

Oily Deposits.

The presence of oil globules carried into the boiler by the condensed steam from the cylinders has been the cause of several boilers collapsing, owing chiefly to overheating of the crown plates of the furnace. Even with good mineral cylinder oils a process akin to steam distillation may take place, so that portions of the oil normally of higher boiling-point than the temperature of the steam are carried forward in the condensed feed-water. These oily globules attach themselves to any precipitated carbonates or sulphates, rendering the material lighter, so that it is carried freely by the convection currents until meeting highly heated metal surfaces it becomes deposited. It is characteristic of such deposits that they occur as frequently on the underside of tubes as on the upper side (where non-oily incrustations are usually much thicker), this being due to this circulating action. Frequently all oil may disappear from the incrustation, owing to excessive heating of the metal in contact with it.

Another action not generally recognised is that some oils derived solely from petroleum (mineral oils) are liable to oxidation with the formation of acids akin to, if not identical with, fatty acids, and these form insoluble soaps with lime and magnesia. With the latter in particular the soap is of an adhesive character, it collects other floating solids, and deposits a mass on plates and tubes. The free acids also attack copper, lead and zinc of brass fittings, and the salts of these metals are frequently found in the incrustation Paul has published analyses of several such deposits, a typical one from a wholly mineral oil being :—

Uncombined oil . . .	49·99	p.c.
Combined oily acids . .	6·72	„
Zinc oxychloride . .	22 79	„
Lead oxide	0 47	„
Copper oxide . . .	0·10	„
Ferric oxide . . .	7 02	„
Magnesium oxide . .	11·90	„
Silica	1·10	„

When mixtures of saponifiable and non-saponifiable oils were employed for cylinder lubrication the formation of fatty acids which passed to the boiler feed water was much more serious, and led to the abandonment of saponifiable oils. With boilers working at the high pressures now common, especially in conjunction with high super-heat of the steam, it has become a most important matter to select only cylinder oils of the highest quality, free from tendency to form acids. In every case where condensed water is used it is most essential to instal efficient means of removing oil, either in exhaust steam separators or feed-water filters. Aluminium sulphate or alum have been employed with success to aid the separation of the emulsified oil, the aluminium hydroxide formed by precipitation with any alkali present collecting the oil globules, and their removal by filtration is facilitated. J. S. S. B.

BOIS-PIQUANT BARK. The bark of *Zanthoxylum caribæum* (Lam.), and *Z. Perrottetii* (D.C.). Used in France as a febrifuge (Heckel a. Schlagdenhaffen, Compt. rend. 98, 996).

BOLDO. A shrub, *Peumus boldus* (Molina), belonging to the *Monimiaceæ*, growing in the Chilian Andes. The bark is used in tanning, the wood makes a good charcoal, and the bark and leaves contain a glucoside $C_{30}H_{52}O_8$, useful as a hypnotic and cholagogue (Chapoteau, Compt. rend. 98, 1052).

BOLE. (*Bol*, Ger.) A ferruginous clay-like substance, of red, brown, or yellowish colour. It is not plastic, and when thrown into water falls to pieces with emission of streams of minute air-bubbles. It has an unctuous feel, and some varieties adhere to the tongue. When cut it presents a shining streak. Before the blowpipe it fuses to a yellowish or white enamel. Its composition is very variable, but its usual limits are from 41 to 47 p.c. SiO_2, 18 to 25 p.c. Al_2O, and 24 to 25 p.c. H_2O, with a proportion of Fe_2O_3, which may reach 12 p.c. It will be noticed that the percentage of water is higher than in clays. The *Fettbol* of Freiberg in Saxony occurs in mineral veins, and contains only about 3 p.c. of Al_2O_3. The bole of Stolpen in Saxony is a yellowish substance containing only a trace of Fe_2O_3. Rammelsberg's analysis yielded SiO_2, 45·92 ; Al_2O_3, 22·14 ; CaO, 3·9 ; H_2O, 25·86. In the 'bole of Sinope' (sinopite) from Asia Minor the SiO_2 falls as low as 32 p.c. The ancients obtained this material from Cappadocia, and used it as a red pigment. It was also employed in medicine as an astringent (*v.* LEMNIAN EARTH).

The following is an analysis of bole, occurring in granite, at Steinkirchen, Bohemia :—Dried at 100° it yielded SiO_2, 46·73 ; Al_2O_3, 26·17 ; Fe_2O_3, 12·34 ; CaO, 1·64 ; MgO, 1·31 ; K_2O, 0·98 ; MnO, 0·28 ; loss on ignition, 10·53 (G. Starkl, Verh. k. k. Geolog. Reichs. Vienna, 1880, 279).

Bole is frequently found as a product of the decomposition of basaltic rocks. Thus the sheets of basalt in N.E. Ireland, representing Tertiary lava-flows, are separated by partings of bole, associated with lithomarge, bauxite, pisolitic iron-ore, and seams of lignite. The Antrim bole is described as a poor variety of aluminous iron-ore (G. A. J. Cole, The inter-basaltic rocks (iron ores and bauxites) of north-east Ireland, Mem. Geol. Survey, Ireland, 1912).

L. J. S.

BOLOGNIAN STONE. A native variety of barium sulphate found as nodular masses embedded in clay near Bologna ; when partially reduced to sulphide by calcination with charcoal it exhibits phosphorescence. Vanino and Zumbusch (J. prakt. Chem. 1911, 84, 305) have attempted to ascertain the factors which determine the phosphorescent quality of Bologna stones. Good samples may vary in sulphur content between 12 and 33 p.c. Marked phosphorescing power seems to depend upon the presence of polysulphides ; products containing only monosulphide are deficient in this respect. The presence of calcium oxide appears to increase the phosphorescing power (*v.* BARIUM and BARYTES).

BOLORETIN *v.* RESINS.

BOMBICESTOROL *v.* STEROLS.

BONE. Bony tissue may be either compact as in the shafts of the long bones, or spongy or cancellated as in the flat bones of the skull and in the extremities of the long bones ; here an external compact layer encloses a mass of spongy bone or diploë. From the embryological point of view, bones may be divided into cartilage bones and membrane bones. The cartilage bones are those which in embryonic life are preceded by cartilaginous prefigurements ; these comprise the majority of the bones in the body, and include all the long bones except the clavicle. In the case of membrane bones (for instance, the flat bones of the cranium), there is no such preliminary cartilaginous prefigurement. It must not, however, be supposed that in the cartilage bones the cartilage is converted into bone ; for here, as in the cases where there is no cartilage present, the true bony tissue is laid down by the agency of certain cells termed osteoblasts in the connective tissue sheath (periosteum) of the bone, and the cartilage when present, after undergoing a certain amount of calcification, is then entirely eaten away by certain large cells called osteoclasts. In the cartilaginous, as distinguished from the bony or teleostean, fishes, the replacement of the cartilage by true bone does not occur.

Bone is deposited in concentric laminæ, the majority of the layers encircling the channels called Haversian canals, in which the blood-vessels lie. The living elements in bone, the bone cells, lie in spaces between the laminæ, and these spaces (lacunæ) intercommunicate by minute canals, in which lymph flows and maintains their nutrition.

The chemical materials present are organic and inorganic. The organic materials are proteins and nucleïn derived from the bone cells, a small quantity of an elastin-like substance which forms a lining to the Haversian canals, and a mucoid or glucoprotein ; but the principal organic material, sometimes misnamed bone cartilage, is better termed osseïn. Osseïn is identical with the collagen of connective tissues, and like it yields gelatin on boiling with water. If the inorganic salts are dissolved out by mineral acids, the osseïn remains as an elastic mass which preserves the original shape of the bone.

The inorganic constituents remain as the so-called bone earth after the bone is completely calcined ; it consists chiefly of calcium phosphate, but also contains calcium carbonate, and small amounts of magnesium, chlorine, and fluorine. Gabriel (Zeitsch. physiol. Chem. 18) states that potassium and sodium also occur. Traces of iron come from the blood in the bone, and of sulphate from chondroitin-sulphuric acid (Mörner, *ibid.* 23).

Investigators differ as to the manner in which the inorganic substances are combined. Chlorine and fluorine are present in the same form as in apatite ($CaFl_2 \cdot 3Ca_3P_2O_8$), and according to Gabriel, the remaining mineral constituents form the combination $3(Ca_3P_2O_8)CaCO_3$. He gives as the simplest expression for the composition of the ash of bones and teeth the formula $Ca_3(PO_4)_2 + Ca_3HP_3O_{12} + H_2O$, in which 2–3 p.c. of the lime is replaced by magnesia, potash, and soda, and 4–6 p.c. of the phosphoric acid by carbon dioxide, chlorine, and fluorine.

Zalesky's analyses (Hoppe-Seyler's Med. Chem. Untersuch. 19) show how closely bone earth agrees in composition in different animals. The figures represent parts per 100. (See Table.) The various bones of the skeleton differ a good deal in the proportion of water, organic solids, and inorganic solids which they contain. This depends to some extent on the admixture of marrow, blood-vessels, and other formations from which it is difficult to free entirely the osseous tissue proper. The quantity of water in fresh bones thus varies from 14 to 44 p.c., and of fat between 1 and 27 p.c. The quantity of total organic substance varies from 30 to 52 p.c., the remainder being inorganic.

—	Man	Ox	Tortoise	Guinea-pig
Calcium phosphate $Ca_3(PO_4)_2$	838·9	860·9	859·8	873·8
Magnesium phosphate $Mg_3(PO_4)_2$	10·4	10·2	13·6	10·5
Ca combined with CO_2, Fl, and Cl	76·5	73·6	63·2	70·3
CO_2 (partly lost on calcining)	57·3	62·0	52·7	—
Chlorine	1·8	2·0	—	1·3
Fluorine	2·3	3·0	2·0	—

The marrow is from the chemical point of view mainly fat; its cells yield protein and nucleoprotein.

On a rough average it may be said that two-thirds of the solids consist of inorganic and one-third of organic compounds.

With regard to the minute composition of bones at different ages, we have no very accurate information. Voit found in dogs and Brubacher in children, that the water in the skeleton decreases and the ash increases with advance of years. Graffenberger's observations on rabbits confirmed this view.

A great many experiments have been made to determine the influence of food—for instance, rich or poor in lime salts—on the composition of bone, but the results have been doubtful or contradictory. The attempts to substitute other alkaline earths for lime have also given uncertain results (*see* H. Weiske, Zeit. f. Biol. 31; also Hammarsten's Physiol. Chem. translated by Mandel).

A large number of data have also been published regarding the variations in chemical composition in different diseases of bone. Thus in exostoses the inorganic material is usually increased; in rickets and osteomalacia, the proportion of water and ossein to bone earth is raised. The view that lactic acid is responsible for the washing out of lime salts from bones in rickets is, however, discredited.

The somewhat rare condition of a curious protein (called Bence-Jones protein, after its discoverer) in the urine is almost invariably associated with bone disease (osteomalacia, or malignant new growths). This protein in many of its characters resembles a proteose, but is probably derived from the mucoid of osseous tissue (Rosenbloom, J. Biol. Chem. 1910, 7, 14; Williams, Bio. Chem. J. 1910, 5, 225).

On heating out of contact with air, bone evolves a large quantity of volatile matter (*v.* Bone oil) which contains ammonia, pyridine bases, pyrrol, nitriles, &c. A black residue is left, consisting of the bone ash in association with carbon, which is called animal charcoal (*q.v.*).

The industrial uses of bone are very numerous and involve a large import trade; not only is the bone itself made into many utensils, but the materials made from the bone (charcoal, bone ash, gelatin, &c.) are put to many uses.

Thus animal charcoal or bone black is employed in many chemical operations, in sugar refining, as a polish for silver work, &c.

Bone meal and bone ash are extensively employed as manure, and in the preparation of the superphosphates of commerce.

The gelatin in an impure form is used in the preparation of paper, silk, furs, &c., and the purer varieties are also put to numerous uses, for instance, as a clarifying agent in the preparation of wines, beers, liqueurs, for food in the preparation of soups, jellies, and puddings, in the making of photographic films, and in Bacteriology for the preparation of culture media. (*See* Merck's Waren-Lexikon, arts. 'Knochen,' 'Knochenasche,' 'Knochenkohle,' 'Knochenöl'; H. Ost, Lehrbuch der Chem. Technologie, 6th ed. 1907, 'Knochenmehl,' 187, 'Knochenleim,' 621; Dammer, Handbuch d. chem. Technologie, 1898, 5, art. 'Knochenverarbeitung,' 254.)

The mention of gelatin as food suggests a word on its nutritive value. It is easily digestible and assimilable, and so is much employed in invalid cookery; nevertheless, it has long been recognised that it is of inferior nutritive value. If animals receive gelatin as their sole nitrogenous food, they waste and die more rapidly than if nitrogenous food is entirely withheld from them; still, when mixed with other proteins, less of the latter is sufficient to maintain life. Recent investigations on the chemistry of proteins have shown that gelatin is destitute of the tyrosine and tryptophane groups, and these groups appear to be of special value or even indispensable for tissue repair; the previously puzzling behaviour of gelatin in nutrition is thus explicable. W. D. H.

BONE ASH *v.* Bone and Fertilisers.

BONE BLACK *v.* Animal charcoal.

BONE EARTH. The calcined residue of bones, consisting chiefly of calcium phosphate (*v.* Bone).

BONE FAT is the fatty matter contained in the bones of animals, and is practically a by-product in the process of working up bones, whether it be for the manufacture of bone char or for the production of glue and gelatin. In either of these manufactures, the 'degreasing' of the bones precedes all further manipulations. Bones from head, ribs, shoulder blades, &c., contain from 12 to 13 p.c. of fat, whilst the 'marrow' bones, *i.e.* the large thigh bones, contain as much as 18–20 p.c. Formerly bone fat was produced by boiling the broken bones with water in open vessels, and allowing the hot liquor to stand, so that the fat could separate on the top and be skimmed off. In the case of fresh bones, the recovered bone fat had a white to yellowish colour, a faint odour and taste, and the consistence of butter. When putrid bones were employed, the bone fat passed, according to age and state of decomposition of the organic matter in the bones, through all gradations from a white fat to a dark rancid fat of a very disagreeable smell. The boiling-out process allows only about one-half of the fat to be recovered. The small yield, and the nuisance connected with the preparation of the bone fat forced the manufacturers to treat the bones with steam under pressure. The broken bones were placed in a cage fixed inside an autoclave, and were heated therein with open steam, under a pressure of 2 to 3 atmospheres. The bone fat so obtained was of the same quality as that prepared by the former process. The best bone fat obtainable in the market is at present prepared by this process, especially in the large packing houses of the United States and South America, where the bones are worked up in the fresh state. They are first washed in 'bone-washing machines.' These are cylinders usually 10 feet long and 3 feet to 4 feet in diameter, built up from iron bars, 1 inch apart, fixed into two cast-iron heads. They are driven by chain and sprocket, and rotate slowly, making about ten revolutions per minute. Through the entire length of the drum there is a hinged door made of bars, which allows the filling and emptying of the cylinder. The machines are usually set at an angle to facilitate the washing and emptying operations. Some manufacturers even resort to steeping the bones in a solution of sulphurous acid in order to obtain a whiter fat (as also a better glue) than unbleached bones afford (*see*, however, Head and Lloyd, J. Soc. Chem. Ind. 1912, 31, 317). The yield of bone fat in the steaming-out process under pressure is considerably higher (by about 50 p c.) than in the boiling-out process in open vessels, so that from bones containing 12 p.c. of fat, 8 to 9 p.c. can be recovered.

Bone fats of this quality can be bleached, but only the best kinds are likely to yield a good product. The higher the percentage of free fatty acids, the greater is the difficulty in bleaching. In fact, products containing more than 50 p.c. of free fatty acids could hitherto not be bleached successfully.

The highest yield of bone fat is obtained by treating the bones with an organic solvent, whereby the animal tissue remains unimpaired, so that the whole of the glue-yielding organic substances can be converted into glue after the fat has been removed. The solvent used in bone-extracting works is almost exclusively petroleum spirit or Scotch shale oil, boiling between 100° and 130°. Proposals have been made to use carbon tetrachloride or chloro- compounds of ethylene and ethane. Experiments with carbon tetrachloride have, however, been abandoned as unremunerative. Extraction with 'benzine' or shale oil takes place in iron digesters under pressure or in open apparatus. The fat obtained by the extracting process is dark-brown, and has a very penetrating, unpleasant smell. In addition to a considerable amount of free fatty acids, it contains lime-soap, calcium lactate, calcium butyrate, and hydrocarbons from the 'benzine' which cannot be fully removed even by prolonged steaming. Hitherto, this kind of fat has not been treated successfully, and even when some immediate improvement was obtained, the colour and also the unpleasant smell 'reverted' after a short time. A patent by Volland (D. R. P. 222669) claims, however, to bleach extracted bone fat by means of barium peroxide.

In von Girsewald's process (Fr. Pat. 430015, 1911) the vapour of the petroleum spirit or other solvent finally remaining in the pores of the material is condensed by the introduction of vapour of the same solvent at a pressure sufficient to produce condensation within the extractor. More complete extraction of the bones is thus effected and the re-admission of air is prevented.

The process patented by Schmidt (Eng. Pat. 5368, 1913) has for its object the rapid separation of water from the solvent. This is effected by condensing the vapours from the extractor in a series of compartments at temperatures just below the boiling-point of the solvent or of the respective fractions, and conducting the condensed liquids to a common separator, where the water is removed prior to the return of the solvent to the extractor.

A method of removing the fat from bones without the use of a solvent is claimed in Powling's process (Eng. Pat. 8397, 1912), the material being agitated in a steam jacketed cylinder until the fat has separated and the water has evaporated.

The bone fat obtained by the boiling-out or steaming-out process can be used for soap making; the fat obtained by the extracting process is utterly unsuitable for that purpose in this country, on account of its rank smell. On the continent, however, such benzine-extracted fat is used up for soap in small quantities, especially when the price of fatty materials is high. The bulk of bone fat is, however, used in candle works, where it is hydrolysed in an autoclave and subsequently subjected to the usual acidifying and distilling processes.

Bone fat is an important article of commerce. The chemical composition of bone fat lies midway between that of marrow fat and tallow. On account of the large amount of fatty acid contained in bone fat, this fat must be examined by special methods, for which the reader is referred to Lewkowitsch, Chemical Technology and Analysis of Oils.

Bone oil, fatty bone oil (not to be confounded with Dippel's oil), is the liquid portion of bone fat which is sometimes prepared in the same manner as tallow oil is obtained from tallow. Bone oil is used as a lubricant, and in the leather industries replaces neat's-foot oil in the preparation of 'fat liquor' and other emulsions. If such bone oil is free from fatty acids, it represents one of the best lubricating oils on account of its very low 'cold test.'

J. L.

BONE MEAL *v.* FERTILISERS.

BONE OIL. *Animal oil*; *Dippel's oil*; *Oil of hartshorn*; *Oleum animale empyreumaticum*; *Oleum cornu cervi*; *Oleum Dippelii.* (*Knochenol*, *Thierol*, Ger.) The product obtained by distilling bones in the preparation of bone black or animal charcoal. The first mention of an animal oil appears to be in the writings of C. Gesner, 1552, and of A. Libavius (Alchemia Lib. II, Tract II.), 1595, whilst J. R. Glauber (1604–1668) also describes the unpleasant-smelling oil derived from the distillation of animal parts. Apparently the first consistent steps in an examination of the oil were made by Johann Dippel in 1711, and afterwards by O. Unverdorben (1826), who isolated from it four bases which he described as *odorin*, *animin*, *olanin* and *ammolin*. The investigations of Anderson (Trans. Roy. Soc. Edin. 1[illegible], 123; 463; 20, 247; 21, 219) were the first in which the pure pyridine bases present in the oil, were obtained.

The bones are first boiled in a large quantity of water, which removes the greater part of the fatty matters; they are then roughly dried and are subjected to dry distillation in iron retorts, similar to those used in the manufacture of coal gas. Bone black or animal charcoal remains behind and bone oil distils. The products of distillation are conducted through long iron tubes, which act as condensers and lead into receivers, where the crude bone oil collects, together with water. The gases are then passed into a separator containing sulphuric acid to retain ammonia, and can afterwards be used for heating purposes, or, if passed through purifiers, for illumination. The crude oil is separated from the aqueous distillate and is subjected to redistillation. The aqueous liquid consists of a solution of ammonium sulphide, ammonium thiocyanate and cyanide, ammonium carbonate, and small quantities of very volatile organic bases. This is treated with sulphuric acid and afterwards distilled with slaked lime The distillate, on treating with solid potash, yields large quantities of ammonia, whilst some oily bases separate out, and are afterwards worked up with the bases contained in the crude oil. This latter is a dark-brown, nearly black liquid, having a fœtid, most offensive smell, and a sp gr. 0·970.

On subjecting it to redistillation it begins to boil at 80°, when quantities of ammonia come over together with an oil. The temperature rises very gradually to about 250°. From 180° upwards large quantities of ammonium cyanide and ammonium carbonate sublime over, and care has to be taken to prevent the condenser being stopped up. A black resinous tar remains, which is employed in making Brunswick black

The following substances have been isolated from bone oil by fractional distillation combined with treatment with acids to separate basic from non basic constituents :—

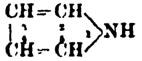
Chief constituents	*Subsidiary constituents*
Butyro nitrile	Methylamine
Valero-nitrile	Ethylamine
Hexo nitrile	Aniline
Isohexo-nitrile	Pyridine
Deco-nitrile	Methyl-pyridine
Palmito nitrile	Dimethyl-pyridine
Stearo-nitrile	Quinoline
Pyrrole	Phenol
Methyl pyrrole	Propionitrile
Dimethyl-pyrrole	Valeramide
Hydrocarbons C_9H_{14}	Toluene
$C_{10}H_{16}$	Ethyl-benzene
$C_{11}H_{16}$	Naphthalene

(Weidel and Ciamician, Ber. 13, 65)

As to the formation of the various compounds in bone oil, the nitriles are formed by the action of ammonia on the fatty acids, pyrrole and the pyrroles are the products of decomposition of the gelatinous substances, and pyridine and its derivatives are condensation products of acrolein, from the dry distillation of the fats, with ammonia, methylamine, &c.

Pyrrole. That portion of the non-basic part of bone oil boiling at 98°–150° contains pyrrole and its homologues. Ciamician and Dennstedt (Ber. 1886, 19, 173) purify the crude pyrrole by heating for many hours under reflux with solid caustic alkali, until the solid mass becomes fused. After cooling, the unaltered oil is separated from the solid residue, and the residue powdered and washed with absolute ether. Water is added and the mass distilled in a current of steam when the pyrrole distils over. The fraction 140°–150° consists of a mixture of homopyrroles—*i.e.* methylpyrroles. That above 150° contains dimethylpyrrole. To separate the α- and β- derivatives, the mixture is converted into the potassium compound by fusion with potash, and heated in a current of carbon dioxide to 200°. Two isomeric homopyrrole carboxylic acids are formed, which differ in the solubility of their lead salts. α-Homopyrrole carboxylic acid melts at 169·5°, and its lead salt is very soluble in water, differing from the β-acid, which melts at 142·1°, and forms a slightly soluble lead salt. The acids obtained respectively yield on distillation with lime the corresponding methypyrroles. α-Homopyrrole boils at 148° under 750 mm. pressure, and β-homopyrrole at 143° at 743 mm.

The constitution of pyrrole is represented as follows :—



$$\left.\begin{array}{l} CH=CH \\ CH=CH \end{array}\right> NH$$

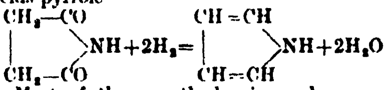
the positions 2 and 5 and 3 and 4 being known as the α- and β- positions respectively. It boils at 130°–131°, and its sp gr is 0·9752 at 12°. Refractive index $\mu_D = 1·5074$ (Gladstone, Chem. Soc. Trans 1884, 246) It is slightly soluble in water, readily soluble in alcohol and ether. It is a weak base, and is only slowly dissolved by dilute acids in the cold, it also possesses faintly acidic properties.

By the action of iodine on potassium pyrrole, tetriodopyrrole is formed, which crystallises in yellowish-brown prisms and decomposes at about 140°. It acts like iodoform as an antiseptic, and is known as iodol. It has the advantage over iodoform of being free from smell.

Pyrrole has been synthesised by passing acetylene and ammonia through red-hot tubes :

$$2C_2H_2 + NH_3 = C_4H_4NH + H_2 ;$$

also by distilling the ammonium salts of mucic and saccharic acids Succinimide, on heating with zinc-dust containing zinc hydrate, also yields pyrrole



$$\left.\begin{array}{l} CH_2—CO \\ | \\ CH_2—CO \end{array}\right> NH + 2H_2 = \left|\begin{array}{l} CH=CH \\ \\ CH=CH \end{array}\right> NH + 2H_2O$$

Most of these methods give only a small yield of pyrrole, but Khotinsky (1909) obtained a 42 p.c. yield by heating ammonium mucate with an excess of glycerol, saturating the mixture with ammonia at 270° and then distilling at 320°–30°.

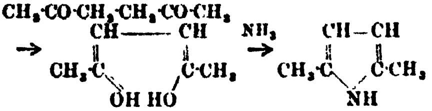
Potassium dissolves in pyrrole with the formation of potassium pyrrole C_4H_4NK, a substance insoluble in ether and decomposed by water into pyrrole and potassium hydroxide. This substance reacts with alkali iodides to form substituted pyrroles ; *e.g.* :

N-Methylpyrrole, $C_4H_4N·CH_3$: boils at 113° ; sp.gr. 0·9203.

N.Ethylpyrrole $C_4H_4N·C_2H_5$: boils at 131° ; sp.gr. 0·9042.

N-Phenylpyrrole $C_4H_4N·C_6H_5$, obtained by distilling the anilides of mucic and saccharic acids, melts at 62°. The homologues of pyrrole contained in bone oil are, however, all substituted in the group C_4H_4.

Pyrrole homologues may be prepared by Paal's method, which consists in the condensation of γ-diketones (*e.g.* acetonyl-acetone) with ammonia :



By the action of benzalchloride on pyrrole in presence of sodium a phenylpyridine is obtained in which the phenyl is in the meta- position to the nitrogen (Ciamician and Silber, Ber. 20, 191).

By reducing pyrrole with zinc and acetic acid Δ^3 pyrroline is produced (Ber. 1901, 3052). Electrolytic reduction to the same substance may be effected by suspending pyrrole in dilute sulphuric acid in the cathode cell of an electrolytic apparatus, the cathode being lead, and passing a current of density 1 amp. per sq. cm. Homologues may be similarly reduced (D. R. P. 127086, 1902). The stronger reduction of pyrrole, by means of hydriodic acid and phosphorus, or by passing pyrrole vapour mixed with hydrogen, over reduced nickel at 180°, converts it into pyrrolidine (tetrahydro pyrrole) C_4H_9N.

Nascent hydrogen converts pyrrole into pyrroline C_4H_6NH, a liquid boiling at 91° which dissolves easily in water. It yields, with nitrous acid, a nitrosoamine $C_4H_6N{\cdot}NO$, m.p. 37°, and on heating with methyl iodide gives methyl pyrroline (Ber. 16, 1536).

Pyrrole is readily oxidised to *maleimide* $C_4H_3O_2N$, which forms faintly yellow crystals, melting at 93°, and readily yields a *dibromide*, melting at 226° under the influence of light and bromine water (Atti. R. 1904, (v.) i. 489).

The action of *formaldehyde* and *methylene chloride* on pyrrole is described by Pictet and Rilliet (Ber. 1907, 1166).

By the action of *chloroform* in absolute ether on the potassium derivative of pyrrole, β-chloropyridine is obtained.

Pyrrole derivatives condense with aldehydes under the following conditions: (1) When the derivatives contain at least one hydrogen atom combined with a carbon atom of the nucleus, either in the α- or β- position; (2) when both α- and β- positions are occupied by substituents, no combination occurs even if the imine hydrogen is present; (3) pyrrole derivatives containing more than one CH group in the ring may combine with aldehydes in molecular proportions (Ber. 1902, 1647). On the constitution of the tripyrrole, obtained by passing dry hydrogen chloride into a benzene solution of pyrrole, *see* Tschelincev, J. Russ. Phys. Chem. Soc. 1915, 47, 1224.

Indole $C_6H_4{<}^{CH}_{NH}{>}CH$ is obtained by dissolving pyrrole in 10 p.c. sulphuric acid, allowing the mixture to stand 1–2 hours, and then distilling in steam after adding excess of sodium hydroxide. Diethyl indole prepared by this process is a viscid ill-smelling oil, boiling at 270°–310° (D. R. P. 125489).

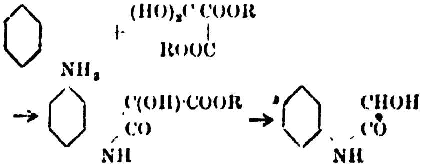
Pyrrole may also be converted into indole by dissolving in dilute hydrochloric acid, adding slight excess of ammonia, filtering, extracting the filtrate twice with ether, and heating the tripyrroline obtained in the extract to above 300°, when indole and pyrrole result (Ber. 1894, 476).

Indole may also be obtained by the reduction of *o*-nitrophenyl acetaldehyde, by fusion of *o*-nitrocinnamic acid with iron and caustic potash

$$NO_2{\cdot}C_6H_4{\cdot}CH:CH{\cdot}CO_2H+2KHO+4H$$
$$=K_2CO_3+3H_2O+C_8H_7N$$

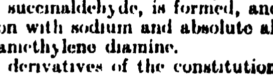
or from *o*-aminophenylacetamide by internal condensation to the amino-indole and subsequent reduction with sodium amalgam (Pschorr).

It crystallises in colourless laminæ, melts at 52°, and is soluble in hot water. It behaves as a feeble base. On treatment with sodium ethoxide and chloroform it is converted into quinoline. The indole molecule is rather difficult to oxidise, without more or less complete decomposition, but if it be first converted into 1-benzoyl indole then on oxidation in acetone solution by potassium permanganate it yields benzoyl anthranilic acid readily, from which anthranilic acid is easily obtained by hydrolysis. In a similar manner halogen substituted indoles can be obtained by the direct action of halogen on the benzoyl indole in carbon bisulphide solution, followed by hydrolysis of the benzoyl group with aqueous ammonia (Weissgerber, Ber. 1913, 46, 651). When large quantities of indole are distilled, a small quantity of high boiling residue is left behind, this is a trimeric form of indole (Keller, Ber. 1913, 46, 726). Substituted indoles may be prepared by the action of heat and a catalyst (zinc chloride or cuprous chloride) on the hydrazones of aldehydes and ketones *e.g.* methyl ethyl ketone phenylhydrazone at 180°-230° with a trace of cuprous chloride yields 2 3 dimethyl indole (Arbuzov, J. Russ. Phys. Chem. Soc. 1913, 45, 70). Primary and secondary amines on condensation with mesoxalic esters also yield substituted indole derivatives; thus from aniline, dioxindole-3-carboxylic acid is obtained, from which dioxindole results on hydrolysis of the carboxylic acid ester in the absence of air (Guyot and Martinet, Compt. rend. 1913, 156, 1625)



Pyrrole may be converted into *tetramethylene diamine* as follows. On treatment with hydroxylamine, a solid compound, probably the dioxime of succinaldehyde, is formed, and this, by reduction with sodium and absolute alcohol, yields tetramethylene diamine.

Pyrrole derivatives of the constitution



have been synthesised from the three nitroanilines by the action of ethylphenacyl acetate (Ber. 1907, 1343).

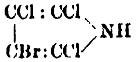
In addition, a large number of pyrrole derivatives has been synthesised by Paal and Braikoff (Ber. 1890, 1086, and also Ber. 1886, 558, 3156).

The physiological action of pyrrole and its derivatives is characterised by their paralysing action on the peripheral nerves connected with the mechanism of the heart. By the introduction of a side group, such as, for instance, the inactive pyridine ring, the physiological effect is greatly intensified. The action of 1-methyl pyrrolidine resembles that of nicotine, atropine, or cocaine, as might be anticipated from their similarity of constitution (Chem. Zentr. 1902, ii. 390).

Chloro- and Bromo- Pyrroles. Sulphuryl chloride in excess acting on an ethereal solution of pyrrole at 0° produces *pentachloropyrrole* in nearly theoretical yield; b.p. 209° or 142°/15 mm. If two molecules only of sulphuryl chloride are used, followed by bromine (2 mols.), *chlorotribromopyrrole* C_4NHBr_3Cl is obtained, which separates from light petroleum in large prismatic masses of a pink colour.

Sulphuryl chloride (3 mols.) followed by bromine (1 mol.) gives *dichlorodibromopyrrole* $C_4HNCl_2Br_2$, which crystallises in large shining scales decomposing just above 100° (Gazz. chim. ital. 1902, 313).

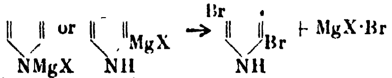
Trichloromonobromopyrrole



$$\begin{array}{ll} CCl:CCl & \\ | & >NH \\ CBr:CCl & \end{array}$$

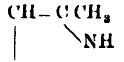
may be obtained by the action of sulphuryl chloride and bromine on ethereal solution of pyrrole at 0°. It crystallises in monoclinic prisms with yellowish-red reflex, turning brown at 105°, and melting and decomposing at 115° (Gazz. chim. ital. 1902, 313; 1904, ii. 178).

Monohalogen derivatives of pyrrole may be prepared by the action of magnesium methyl iodide on a secondary pyrrole, followed by halogen at low temperature (Hess and Wissing, Ber. 1914, 47, 1416)



These compounds are very unstable, and decompose even on keeping; thus, bromopyrrole explodes violently even when kept in a sealed tube, decomposing into carbon and ammonium bromide.

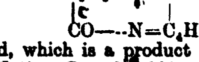
The **dimethylpyrrole** contained in the fraction of bone oil boiling above 150° has been obtained synthetically as follows: By the action of ammonia on diacetosuccinic ether, the ether of dimethylpyrrole dicarboxylic acid is obtained This, on saponification, yields the acid, and, on heating, carbon dioxide is split off, leaving dimethylpyrrole. It has the composition



$$\begin{array}{ll} CH-C\,CH_3 & \\ | & \diagdown NH \\ CH=C{\cdot}CH_3 & \end{array}$$

and is an almost colourless oil boiling at 165°. It is very volatile with steam, colours a pine splint an intense red, and yields on boiling with acids a pyrrole-red similar to other pyrrole homologues.

Pyrrolecarboxylic acids $C_4(NH)H_3CO_2H$. The α-acid is obtained from α-homopyrrole by fusion with potash or by the action of tetrachloride of carbon and alcoholic potash on pyrrole. It melts at 191°, and differs from the β- acid in forming a soluble lead salt. On heating with acetic anhydride, the substance pyrocoll



$$\begin{array}{l} C_4H_3=N-CO \\ |\qquad\qquad\quad | \\ CO-N=C_4H_3 \end{array}$$

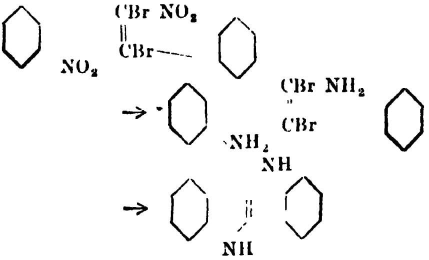
is formed, which is a product obtained by distilling gelatine (Ber. 17, 103).

β-Pyrrolecarboxylic acid is formed by fusing β-methylpyrrole with potash. It crystallises in fine needles, melting at 162°, and forms an insoluble lead salt.

N-Acetylpyrrole $C_4H_4N{\cdot}C_2H_3O$, obtained by the action of acetyl chloride on potassium pyrrole, is an oil boiling at 178°. It is decomposed by alkalis into pyrrole and acetic acid (Ber. 16, 2352).

C-Acetylpyrrole $C_4H_3(C_2H_3O)(NH)$ is formed, together with the foregoing, by acting on pyrrole with acetic anhydride. It melts at 90° and boils at 220°, but is not decomposed by alkalis.

A di-indole has been obtained from di-(ortho-nitrophenyl-bromo) ethylene by reduction with stannous chloride to the corresponding di-amino compound, followed by elimination of hydrobromic acid, first by boiling for a short time with alcoholic picric acid and subsequently with alcoholic potash (Ruggli, Ber. 1917, 50, 883).



Pyridine C_5H_5N is contained in that fraction of the basic oils of bone oil which boils below 120°, but is also found in smaller quantities in the higher fractions. It can be separated in these by means of its picrate

$$C_5H_5N,C_6H_2(NO_2)_3OH$$

which melts at 162°. It is not easily acted on by oxidising agents, and can be separated by this means from the other components of the fraction.

It is formed from all pyridinecarboxylic acids by distilling with lime.

The following are some of the synthetic methods for preparing pyridine and its homologues:—

1 Hydrocyanic acid and acetylene when passed through a red-hot tube yield pyridine

$$2C_2H_2+HCN=C_5H_5N$$

(Ramsay, Ber. 10, 736).

2. Isoamyl nitrate when heated with phosphoric anhydride yields pyridine

$$C_5H_{11}ONO_2+3P_2O_5=C_5H_5N+6HPO_3$$

(Chapman and Smith, Ann. Suppl. 6, 329).

3. Acrolein ammonia, on heating, gives off water yielding methylpyridine

$$C_6H_9NO=C_5H_4(CH_3)N+H_2O$$

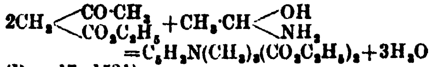
4. The same compound is formed by heating allyl tribromide with alcoholic ammonia at 250°

$$2C_3H_5Br_3+NH_3=C_5H_4(CH_3)N+6HBr$$

5. Glycerol and acetamide, on heating with phosphorus pentoxide, yield methylpyridine (Ber. 15, 528).

6. Potassium pyrrole, on heating with chloroform, yields chloropyridine.

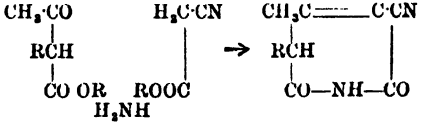
7. Ethyl acetoacetate, heated with aldehyde ammonia, gives dihydrocollidine dicarboxylic ester



$$2\mathrm{CH_2}\!\left\langle\begin{matrix}\mathrm{CO\cdot CH_3}\\ \mathrm{CO_2C_2H_5}\end{matrix}\right. + \mathrm{CH_3\cdot CH}\!\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{NH_2}\end{matrix}\right. = \mathrm{C_5H_2N(CH_3)_3(CO_2C_2H_5)_2} + 3\mathrm{H_2O}$$

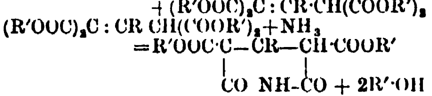
(Ber. 17, 1521).

8. Guareschi has obtained compounds of the pyridone type by condensing alkyl aceto-acetic esters with cyanacetic esters and ammonia



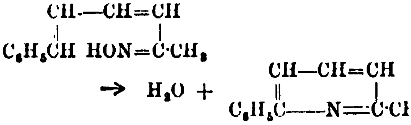
9. Ruhemann has also obtained the pyridone type by the condensation of alkyl dicarboxyglutaconic esters with ammonia

$$\mathrm{RCCl_3} + 3\mathrm{CHNa(COOR')_2} = \mathrm{CH_2(COOR')_2} + 3\mathrm{NaCl} + \mathrm{(R'OOC)_2C:CR\cdot CH(COOR')_2}$$



$$\mathrm{(R'OOC)_2C:CR\,CH(COOR')_2} + \mathrm{NH_3} = \mathrm{R'OOC\cdot C{-}CR{-}CH\cdot COOR'} \; (\mathrm{CO\;NH{-}CO}) + 2\mathrm{R'\cdot OH}$$

10. Cinnamenylidine acetoxime on distillation is converted in α-phenyl-α′-methyl pyridine



11. Pyridine bases are obtained by the condensation of ketones with acid amides (Pictet and Stehelin, Compt. rend. 1916, 162, 867); thus by heating acetone (2 mols.) with acetamide (1 mol.) at 250°, 2.4.6-trimethyl pyridine is formed, whilst triphenyl pyridine results similarly from acetophenone and benzamide.

By heating a mixture of glycerol and ammonium phosphate, a mixture of a large number of pyridine bases is formed. β-methyl, β-ethyl, probably β-propyl, pyridine, besides pyridine itself and homologues of the diazine $C_4H_4N_2$, have been recognised (Stoehr. J. pr. Chem. 1892, 20).

Pyridine is a liquid with a pungent smell, miscible with water; sp. gr. 0·9855 at 15°, and 0·9944 at 4°; and boils at 115·2°/760 mm. It forms a hydrochloride C_5H_5N,HCl, and a platinichloride $(C_5H_5NHCl)_2PtCl_4$. Sodium amalgam yields piperidine, *i.e.* hexahydropyridine, which is reconverted into pyridine on oxidation. It forms an ammonium iodide with alkyl iodides, and with chloracetic acid a pyridine-betaïne $\mathrm{C_5H_5N}\!\left\langle\begin{matrix}\mathrm{CH_2}\\ \mathrm{O}\end{matrix}\right\rangle\mathrm{CO}$. By the action of sodium on pyridine a dipyridine $C_{10}H_{10}N_2$ is obtained, an oil boiling at 280°–281°/744 mm., which on oxidation with permanganate yields *iso*nicotinic acid. Together with dipyridine, a body *p*-dipyridyl is formed $NC_5H_4\cdot C_5H_4N$, which melts at 114° and distils at 304°. It also yields *iso*nicotinic acid on oxidation, and on reduction with tin and hydrochloric acid forms *iso*nicotine, which melts at 78° (Ber. 16, 423).

Sodium reacts with pyridine at ordinary temperature (best in an atmosphere of nitrogen) to form dipyridine sodium $(C_5H_5N)_2Na$, which on heating to 130° is transformed into pyridine sodium $C_5H_5N\cdot Na$ (B. Emmert, Ber. 1914, 47,

The isomeric *m-dipyridyl* is obtained from *m*-dipyridyldicarboxylic acid (by oxidising phenanthroline). It boils at 293°, and yields on reduction with tin and hydrochloric acid *nicotidine* $C_{10}H_{14}N_2$, which boils at 228° (Ber. 16, 2521).

Piperidine between 180° and 250° is converted into pyridine in presence of nickel; pyridine when passed together with hydrogen over reduced nickel at 160°–180°, yields amylamine not piperidine, and this in poor yield. At higher temperatures ammonia, pentane and lower hydrocarbons are obtained (Sabatier and Mailhe Compt. rend. 1907, 784).

Pyridine may advantageously be employed as a halogen carrier in halogenation of aromatic compounds (Cross and Cohen, Chem. Soc. Proc. 1908, 15).

The compound of pyridine with methy iodide, when added to a solution of the necessary amount of iodine in alcohol, is converted into pyridine methylpentiodide $C_5H_5N(MeI)I_4$ melting at 47·5°. Various other periodides are described by Prescott and Trowbridge (J. Amer. Chem. Soc. 1895, 859).

Acetyl and benzoyl chlorides if quite pure do not react with pyridine in the presence of anhydrous aluminium chloride, but if a trace of thionyl chloride be introduced, then the norma ketone production takes place (Wolffenstein and Hartwich, Ber. 1915, 48, 2043).

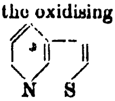
Double compounds with zinc bromide nickel bromide, copper bromide, and silver iodide, are formed, but are rather unstable (Compt. rend. 1891, 622).

The physiological action of pyridine is similar to that of piperidine, but more energetic. Both produce paralysis of the motor nerves, by their effect on the motor centres. There are also destructive changes in the blood corpuscles, and paralysis of the heart, especially in pyridine poisoning (Chem. Soc. Abstr. 1891, 603). It is excreted as methylpyridylammonium hydroxide (Chem. Soc. Abstr. 1893, ii. 544).

The double compound of pyridine with silver nitrate $AgNO_3\cdot 2C_5H_5N$ has been recommended by Witt as a ripening agent for photographic emulsions (J. Soc. Chem. Ind. 1904, 235). Luppe-Cramer, however, denies that it has any advantages over the ordinary ammonia ripening (*ibid.* 1906, 197).

Sulphurous acid esters of pyridine, which may be obtained by heating under a reflux condenser with excess of a bisulphite solution, are useful in the preparation of dyestuffs, and are also used as medicaments (D. R. P. 208638).

A pyridine-2.3-thiophen has been obtained in small quantity by the application of the Skraup reaction to 2-aminothiophen; using 2-nitrothiophen as the oxidising agent



(Steinkopf and Lutzendorff, Annalen, 1914, 403, 45).

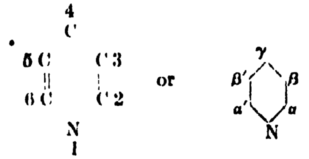
On heating pyridine with concentrated sulphuric acid to 300°, β-pyridine-sulphonic acid is obtained. The sodium salt of this acid, distilled with potassium cyanide, yields β-pyridyl cyanide, which on hydrolysis forms nicotinic

Sulphonation of the pyridine nucleus can be carried out more readily in the presence of vanadyl sulphate.

Pyridine may be directly nitrated by heating with a mixture of fuming nitric and fuming sulphuric acids. Pyridine nitrates more readily if an amino group is present, *e.g.* 2-aminopyridine nitrates nearly as readily as aniline. The nitro pyridines resemble the nitro-anilines, are yellow in colour and feebly basic.

Pyridine may be estimated in aqueous solution by heating with excess of gold chloride and dilute HCl, evaporating to dryness and heating the ppt. after repeated washing with pure dry ether. The ppt. has the composition $C_5H_5N \cdot HCl \cdot AuCl_3$ (Compt. rend. 1903, 324).

Pyridine can be represented as a benzene ring in which one CH group is replaced by nitrogen according to the following scheme:—



The positions 2, 6, and 3, 5 are known as ortho- and meta-, and 4 as the para- position. Hence three mono- derivatives of pyridine are possible. The position of the substituting groups in these isomerides has been proved by means of the phenylpyridines obtained from the naphthaquinolines (Monatsh. 4, 437; Ber. 17, 1518).

HYDROXY- DERIVATIVES OF PYRIDINE.

The three possible hydroxypyridines are known:—

α-**Hydroxypyridine,** α-**pyridone,** by distilling the silver salt of hydroxyquinoline acid; melts at 107°, and is coloured red by ferric chloride.

β-**Hydroxypyridine** is formed from the β sulphonic acid by fusing with potash. It melts at 123°, and is also coloured red by ferric chloride.

γ-**Hydroxypyridine** or γ-**pyridone** (which is probably not a hydroxyl- but a carbonyl compound) is obtained from hydroxypicolinic acid with evolution of CO_2. It melts at 148° or at 62° in the hydrated form, and is coloured yellow by ferric chloride (Ber. 17, Ref. 169).

AMINO- PYRIDINES.

Of the three possible aminopyridines, two have been definitely isolated.

1.—*Aminopyridine* is formed by the distillation of 2-aminopyridine-5-carboxylic acid. It melts at 56° and boils at 204°. It is not diazotisable, but on treatment with concentrated hydrochloric acid and nitrous acid yields 2-chloropyridine.

2.—*Aminopyridine* is formed by the action of sodium hypobromite on the amide of nicotinic acid, or by the action of sodamide on pyridine below 120°, and decomposition of the resultant product with water; the further action of sodamide yields 2·6-di-aminopyridine, which couples with diazo-compounds (Tschitschibabin, J. Russ. Phys. Chem. Soc. 1914, 46, 1216). It melts at 62° and boils at 250°–252°. It is a diazotisable base.

PYRIDINE MONOCARBOXYLIC ACIDS $C_5NH_4(CO_2H)$.

α-**Pyridinecarboxylic acid** (2- or ortho-), *picolinic acid* was first obtained by oxidising α-picoline. It is easily soluble in water, crystallises in white needles, melts at 137°, and sublimes. By the action of sodium amalgam, ammonia is given off with the formation of an acid $C_6H_8O_3$ (oxysorbinic acid).

β-**Pyridinecarboxylic acid** (3- or meta-), called *nicotinic acid* from the fact of being first obtained by oxidising nicotine, is also obtained from β-methyl- or ethyl-pyridine, from β-pyridyl cyanide, and from three dicarboxylic acids of pyridine (quinolinic acid, cinchomeronic acid, and *iso*cinchomeronic acid), which on heating give off carbon dioxide. It crystallises in needles and melts at 232°. It is readily soluble in hot water and in alcohol, but is insoluble in ether.

γ-**Pyridinecarboxylic acid** (4- or para-), *isonicotinic acid* is obtained from cinchomeronic acid and 2 : 4-pyridinedicarboxylic acid on heating, and also by the oxidation of all γ-substituted pyridines. It melts at 299 5° with sublimation or at 315° in a closed tube, and crystallises from hot water in fine needles.

HYDROXYPYRIDINE-MONOCARBOXYLIC ACIDS.

Several of these acids have been prepared either synthetically, *e.g.* by heating komanic acid $C_6H_4O_4$ with ammonia, or from the dicarboxylic acids by splitting off 1 mol. of carbon dioxide (Ber. 17, 589).

Komenaminic acid $C_5NH_2(OH)_2COOH,2H_2O$ is obtained by boiling komenic acid $C_6H_4O_5$ with ammonia. It decomposes at 270° into carbon dioxide and dihydroxypyridine.

PYRIDINE-DICARBOXYLIC ACIDS $C_5NH_3(CO_2H)_2$.

The acids of this type may be obtained as follows:—

1. By the oxidation of disubstituted pyridines, containing aliphatic side chains; or of monosubstituted monocarboxylic acids.
2. By heating the tricarboxylic acids.
3. By the oxidation of quinoline and its homologues.
4. By the oxidation of various alkaloids (cinchonine, cinchonidine, &c.).

Quinolinic acid (αβ- or 2 : 3-) is formed by oxidising quinoline. It decomposes and softens at 190°–195°, solidifies at 200°, and melts again at 231°. It decomposes on heating into carbon dioxide and nicotinic acid.

Cinchomeronic acid (βγ- or 3 : 4-) is formed by the oxidation of the quinine alkaloids with nitric acid, or from βγ-methylpyridinecarboxylic acid on oxidation with permanganate. It melts at 259°, decomposing into carbon dioxide, *iso*nicotinic acid, and some nicotinic acid.

Lutidinic acid (αγ- or 2 : 4-) is obtained, together with some *iso*cinchomeronic acid, by oxidising lutidine. It melts at 239°–240° (Voigt, Annalen, 228, 54), 235° (Ladenburg, Annalen, 247, 27), decomposing into carbon dioxide and *iso*nicotinic acid.

***Iso*cinchomeronic acid** (βα′-) melts at 236°, decomposing into carbon dioxide and nicotinic acid (Werdel and Herzig, Wiener Akad. B. 1879, 825).

Dicarboxylic acid ($\beta\beta'$-) or **Dinicotinic acid**. By heating to 150° *s*-pyridine tetracarboxylic acid obtained by oxidising the lutidinecarboxylic acid, prepared by the condensation of *iso*butaldehyde ethylacetoacetate and ammonia. The acid does not melt at 285° (Hantzsch and Weiss, Ber. 1886, 19, 284).

Dicarboxylic acid (aa'-) or **Dipicolinic acid.** Obtained by oxidising 2 : 6-dimethylpyridine. It melts at 243° (Epstein, Annalen, 231, 32), decomposing into carbon dioxide and pyridine.

Hydroxypyridine-dicarboxylic Acids
$C_5NH_2(OH)(CO_2H)_2$.

Hydroxyquinolinic acid [$OH : (CO_2H)_2 = (a' : a : \beta)$]. By fusing quinolinic acid with potash. It blackens without melting at 254° (Ber. 16, 2158). Heated with water to 195° it decomposes into carbon dioxide and hydroxypyridinecarboxylic acid. Its silver salt on heating yields a-hydroxypyridine (Ber. 17, 590).

Ammoniochelidonic acid is obtained by heating chelidonic acid with ammonia.

Pyridine-tricarboxylic Acids $C_5NH_2(CO_2H)_3$.

$a\beta\gamma$-**Tricarboxylic acid, Carbocinchomeronic acid**, is formed by completely oxidising the quinine alkaloids, also from γ-methylquinoline and from γ-quinolinecarboxylic acid. It loses $1\frac{1}{2}H_2O$ (of crystallisation) at 115°-120°, and melts, if quickly heated, at 250° (Annalen, 204, 308).

$a\beta\beta'$-**Tricarboxylic acid, Carbodinicotinic acid**, is obtained from β-quinolinecarboxylic acid.

The six tricarboxylic acids theoretically possible are known and characterised.

Pyridine tetracarboxylic Acids
$C_5NH(CO_2H)_4$.

$a\beta a'\beta'$-**Tetracarboxylic acid.** By oxidising the lutidinedicarboxylic acid formed by the condensation of *iso*butylaldehyde with ethyl acetoacetate and ammonia (Hantzsch and Weiss, Ber. 19, 284).

The acid obtained by oxidising collidinemonocarboxylic acid crystallises with 2 molecules of water. It does not possess basic properties. Energetic oxidation converts it into oxalic acid.

Pyridine-pentacarboxylic acid $C_5N(CO_2H)_5$ from trimethylpyridine-dicarboxylic acid. Crystallises from water with $3H_2O$. Decomposes without melting about 200°.

Halogen Derivatives of Pyridine.

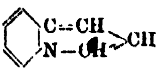
a-Chloropyridine results from the action of PCl_5 on a-hydroxypyridine; is an oil boiling at 166°/714 mm. (Ber. 1891, 3150).

β-Chloropyridine By the action of chloroform or carbon tetrachloride on potassium pyrrole (Ber. 14, 1153) is an oil; b.p. 148°/743 mm.

Dichloro- and trichloro-pyridine are known.

A *dibromopyridine* ($\beta\beta'$) has been obtained by acting on collidine-dicarboxylic acid with bromine and afterwards removing the carboxyl-groups (Pfeiffer, Ber. 20, 1349). It is identical with that obtained by acting on pyridine with bromine (Hofmann, Ber. 12, 988).

a-Picoline is transformed by acetic anhydride into *picolide* $C_{12}H_{14}O_2N$, which on heating with hydrochloric acid yields *pyrindole* C_8H_7N, an isomeride of indole.



(Scholtz and Fraude, Ber. 1913, 46, 1069).

Homologues of Pyridine.

Picoline (*a-methylpyridine*) $C_5NH_4(CH_3)$. This base is separated from that portion of bone oil which boils between 130° and 145°. On subjecting this to redistillation, the greater part of the oil comes over between 133° and 139°. It is not possible to effect a separation of the bases by means of fractional distillation, but a difference in the solubility of the platinum salts of the two bases furnishes a means of separating them. According to Ladenburg (Ber. 1885, 47), commercial picoline consists of three bases: a-methylpyridine, a little β-methylpyridine, and probably aa'-dimethylpyridine. The same observer (Ber. 1885, 51) has also noticed the presence of pyridine in this fraction. It can be separated by means of its picrate, which melts at 162°.

Picoline boils at 128.8°/760 mm.; is an optically inactive oil, and on oxidation yields picolinic acid (*v. supra*).

β-Methylpyridine may be synthetically prepared by heating acetamide with glycerol and phosphoric anhydride. It boils at 143·5°, and on oxidation yields nicotinic acid. It also differs from the a-derivative in being slightly lævorotatory. Landolt shows this effect to be due to errors in manipulation (Ber. 1886, 157).

γ-Methylpyridine does not appear to be contained in bone oil. It has been obtained synthetically by the action of heat on acroleïn-ammonia, and also from allyl tribromide; b.p. 143·1°/760 mm.

Picoline monocarboxylic Acids
$C_5NH_3(CH_3)CO_2H$.

Picolinecarboxylic acid (*pyridine-a-methyl-γ-carboxylic acid*) is formed from uvitonic acid, the product of condensation of pyruvic acid and ammonia. It sublimes without melting, and yields on oxidation $a : \gamma$-pyridinedicarboxylic acid.

$\beta\gamma$-**Methylpyridine carboxylic acid** ($CH_3 \cdot CO_2H - \gamma : \beta$) is obtained by heating methylquinolinic acid to 180°-185°. It melts at 212° (Ann. Chim. Phys. [5] 27, 493), and yields on oxidation cinchomeronic acid.

Six of the ten possible picoline monocarboxylic acids are known and characterised.

Picoline-dicarboxylic Acids
$C_5NH_2(CH_3)(CO_2H)_2$.

Methylquinolinic acid ($(CO_2H)_2 : CH_3 = a\beta\gamma$). By oxidising γ-methylquinoline with permanganate. It melts at 186°, giving carbon dioxide and γ-methyl-β-pyridine-carboxylic acid.

Uvitonic acid [$(CO_2H)_2 : CH_3 = a\gamma a'$] is the condensation product obtained from pyruvic acid and alcoholic ammonia. It melts at 274°, splitting up into carbon dioxide and picolinecarboxylic acid.

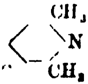
Picoline-dicarboxylic acid, from aldehydine, the condensation product of ethylidine chloride and aldehyde ammonia. It sublimes easily without melting.

Three other isomerides are known.

A picoline-tetracarboxylic acid is also obtainable from the dicarboxylic acid of collidine by oxidation of the methyl- groups with permanganate. Lutidine-tricarboxylic acid is formed as an intermediate product

Lutidine (*dimethylpyridine*). The bases having this constitution are mainly contained in that portion of the basic oil boiling between 150°–170°. After redistilling, it is separated into the two fractions 150°–160° and 160°–170°. The position of the methyl groups in these two fractions is determined by means of the oxidation products formed. The first fraction yields on oxidation *iso*cinchomeronic acid, which melts at 236°. On heating, carbon dioxide is split off and nicotinic acid is formed. From this is inferred that the position of the two methyl groups is $\alpha'\beta$. The higher fraction yields lutidinic acid on oxidation, and this, on heating, gives *iso*nicotinic acid, from which it follows that the methyl- groups have the positions $\alpha\gamma$. All the acids give pyridine on distillation with lime. According to the researches of Ladenburg and Roth (Ber. 18, 49), the fraction 139°–142° also contains a lutidine, which was separated by means of the mercuric chloride salt, melting at 186°. This was decomposed with potash, and distilled, when, after drying, an oil was obtained which boiled at 142°–143°, and yielded on oxidation with permanganate a dibasic acid which is identical with that obtained from synthetical lutidine prepared by condensing cinnamic aldehyde, ethyl acetoacetate, and ammonia (Epstein, Annalen, 231, 1). Its sp gr. is 0 9545, and b.p. 143°.

The constitution of the β lutidine is



(Ladenburg and Roth).

By distilling dimethyl pyridine dicarboxylic acid with lime a 91 p.c. yield of 2 · 6-lutidine can be obtained This method appears to be the most convenient way of preparing pure lutidine (Mumm and Hüneke, Ber. 1917, 50, 1568; 1918, 51, 150).

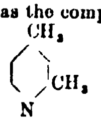
The isomeric α, β and γ-ethyl pyridines are also known, the β and γ-forms being produced when cinchonine or brucine are distilled with caustic alkali, and the α-form on heating pyridinium ethyl iodide to 290°.

Lutidine-monocarboxylic acid (*$\alpha\alpha'$-dimethylnicotinic acid*). Obtained by distilling lutidine-dicarboxylic acid (Weiss, Ber. 19, 1308). It crystallises in fine needles melting at 160°.

Lutidine-dicarboxylic acid (*$\alpha\alpha'$-dimethyl-$\beta\beta'$-dicarboxylic acid*). Obtained by the condensation of *iso*butylaldehyde, ethyl- aceto-acetate, and ammonia (Engelmann, Annalen, 231, 51; Hantzsch and Weiss, Ber. 19, 284).

Lutidine-tricarboxylic acid (*$\alpha\gamma$-dimethyl-$\beta\alpha'\beta'$-tricarboxylic acid*) is formed by the oxidation of collidine-dicarboxylic acid with permanganate.

α-Lutidine (2 : 4-*dimethylpyridine*). Separated by adding mercuric chloride to a solution in hydrochloric acid of the bases boiling at 158°–160°. The salt has the composition $C_7H_9N,HCl,2HgCl_2$, and melts at 127°. On distilling with potash, the salt is decomposed, and the base, after drying, boils at 157°. Its sp.gr. is 0 9493 at 0°/4°. It yields a pyridine-dicarboxylic acid on oxidation with permanganate, and the acid melts at 235°. This is known as α-lutidinic acid or $\alpha\gamma$-pyridine-dicarboxylic acid, since on heating carbon dioxide is given off and *iso*nicotinic acid is formed. Hence α-lutidine has the composition

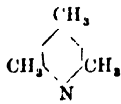


(Ladenburg and Roth, Ber. 18, 913).

Collidines (*γ-collidine, trimethylpyridine*)

$C_5NH_2(CH_3)_3$

may be prepared by distilling collidine dicarboxylic ester (obtained by oxidising the condensation product of aldehyde ammonia and ethyl acetoacetate) with lime. It boils at 171°–172°, and has the constitution



A base, $C_8H_{11}N$, has been isolated from the fraction of bone oil boiling between 170° and 180°, but this has been shown by Weidel and Pick to be a 2-methyl-4-ethylpyridine from the fact of its giving on oxidation lutidinic acid melting at 219°. The base is more soluble in cold than in hot water. Its sp gr. is 0 9286 at 16 8°; it boils at 177 8°/758 mm. (Weidel and Pick, Monatsh. 5, 656). These authors are of opinion that Anderson's collidine (Phil. Mag. 4, 9, 145, 214) was impure. The base does not form any crystallised salts, and is not identical with any synthetical collidine.

Aldehydine (2 *methyl-5-ethylpyridine*). Formed by the condensation of ethylidene chloride with ammonia (Durkopf, Ber. 18, 921), by heating an alcoholic solution of aldehyde-ammonia to 120° (Baeyer and Ader, Annalen, 155, 294), and as a decomposition product of cinchonine or brucine when these alkaloids are distilled with caustic alkali It boils at 176°, and has sp.gr 0 9389 at 0°/4°.

Of the isomerides of collidine, α-normal propyl pyridine (conyrine) is of considerable theoretical importance, owing to its relationship with the alkaloid conine (*q v.*).

Collidine dicarboxylic acid is obtained by oxidising hydrocollidine-dicarboxylic acid with nitrous acid. The ester of the latter acid is the product of condensation of ethyl acetoacetate with aldehyde ammonia. It yields on heating with lime $\alpha\alpha'\gamma$-trimethylpyridine. The acid yields by successive oxidation of the methyl-groups by permanganate the following carboxylic acids:

Lutidine-tricarboxylic acid

$C_5N(CH_3)_2(CO_2H)_3$,

Picoline-tetracarboxylic acid

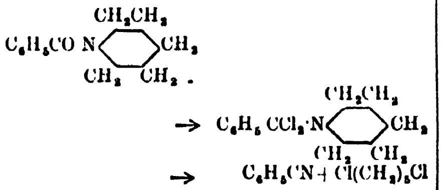
$C_5N(CH_3)(CO_2H)_4$.

Pyridine-pentacarboxylic acid $C_5N(CO_2H)_5$.

If one carboxyl- group be removed from the original acid and then it be oxidised, the following acids are successively obtained:—

From collidine-monocarboxylic acid $C_5NH(CH_3)_3CO_2H$ the acids lutidine-dicarboxylic acid $C_5NH(CH_3)_2(CO_2H)_2$, picoline-tricarboxylic acid $C_5NH(CH_3)(CO_2H)_3$, pyridine-tetracarboxylic acid $C_5NH(CO_2H)_4$.

Piperidine, hexahydro-pyridine, is obtained in small quantity by the reduction of pyridine with tin and hydrochloric acid (Konigs, Ber. 1881, 14, 1856). A better yield is obtained by operating in absolute alcoholic solution with sodium. It may be prepared from pyridine in 95 p.c. yield by electrolytic reduction (E. Merck, D. R. P. 90308; Pip, Eng. Pat. 21471). It may also be prepared by heating piperine, obtained from pepper, with soda lime, or by the reduction of trimethylene cyanide in alcoholic solution with sodium. It is a liquid smelling like pepper and ammonia, boiling at 105·7°, sp.gr. 0·8810 at 0°. Miscible in all proportions with water. It combines with quinones to form dyes. J. v. Braun (1904) has shown that by benzoylation of piperidine and subsequent heating with phosphorus pentachloride to 250° the cyclic system is destroyed and a good yield of pentamethylene dichloride is obtained, such 1·5-dichloro-compounds being very difficult to obtain by ordinary synthetic methods.



Its combination with hydroquinone, pyrocatechin, and several other phenols, has been patented by Joseph Turner & Co., Ltd. (D. R. P. 98465).

An account of the physiological action of piperidine and allied compounds is given by Wolffenstein (Ber. 34, 2410).

Piperidine guaiacolate prepared by the action of piperidine on guaiacol dissolved in benzene or petroleum melts at 79·8°. It is used in the treatment of phthisis (Pharm. J. 1897, 81), and is important as combining the properties of a strong vascular and nervine tonic—piperidine—with an antiseptic guaiacol (Tunnicliffe, Chem. Soc. Trans. 1898, 145).

Various derivatives of piperidine have been synthesised by Ahrens (Ber. 1898, 2278).

Quinoline. *See* QUINOLINE.

COLOURING MATTERS DERIVED FROM BONE-OIL BASES.

1. **From Pyrrole.** A red dye may be obtained from pyrrole by treating cotton cloth, after dipping in a weak alcoholic solution of bitter almond oil (benzaldehyde), with alcoholic pyrrole solution, hydrochloric acid, ferric chloride, and gently warming. A black colour is obtained by substituting cinnamon oil (cinnamic aldehyde) (Chem. Zeit. 1890, 348).

Pine wood may be dyed red by moistening with hydrochloric acid, and treating with the vapour of pyrrole.

Pyrrole blue may be obtained in two varieties: (*a*) by mixing pyrrole and isatin (1 mol. of each) in sulphuric acid, yielding the 'A' variety; and (*b*) by operating in acetic acid under specified conditions, when pyrrole blue 'B' is obtained with a certain amount of A. Pyrrole blue B has a metallic lustre, and is much less soluble than pyrrole blue A. Pyrrole blue A cannot be acetylated, but on treating pyridine solution with acetic anhydride a small amount of the pyrrole blue B derivative is obtained. This acetyl derivative dissolves in sulphuric acid to a magenta solution, which rapidly changes to a cornflower blue, owing to the formation of a disulphonic acid. This acid is very soluble in water and dyes silk blue (Liebermann and Hase, Ber. 1905, 2847; *see* also Ber. 17, 1034).

2. **From Pyridine.** Pyridine dyestuffs may be obtained by diazotising aminobenzyl pyridine, and combining with the usual components. Aminobenzylpyridine is obtained by reducing the nitro- compound produced by the condensation of nitrobenzyl chloride and pyridine bases. These products dye tannin-mordanted cotton, or wool and cotton from an acid-bath (Farb. vorm. Meister, Lucius and Bruning, Eng. Pat. 4545).

When mixtures of pyridine (1 mol.) and aromatic amines (2 mols.) are acted upon by cyanogen chloride or bromide dyestuffs are formed practically quantitatively and very pure, with the elimination 1 mol. of cyanamide. They crystallise well, and vary from yellow, through orange and red, to violet, and dye silk in shades showing fine fluorescence; and some show marked affinity for unmordanted cotton. They are soluble in water with difficulty, more readily in acetic acid and alcohol, and in pyridine (W. König, J. pr. Chem. 1904, 105).

3. **From Piperidine.** The quinones (benzo-, tolu-, naphtha-, phenanthra-quinones) interact with piperidine, yielding colouring matters which are readily changed by acids and alkalis. The compound with benzoquinone $C_6H_2O_2(NC_5H_{10})_2$ forms thick, reddish-violet prisms with blue reflex, melting at 178°. Neutral or alkaline solutions are blood-red, acid solutions carmine (Lachowicz, Monatsh. 1888, 505).

Isatin blue is derived from piperidine as follows: Dipiperidyl isatin is prepared by heating an alcoholic solution of isatin (1 mol.) with (2 mols.) piperidine on the water-bath for an hour, and crystallising from alcohol. Isatin blue results from heating this compound to 125°–160° in a current of air, or by agitating with acetic anhydride at 60° for some time and pouring into water. It forms indigo-blue solutions in alcohol, ether, or acetic acid, and is insoluble in benzene or chloroform. It may be heated without change to 160°, but is completely decomposed at 230° (Schotten, Ber. 1891, 1366).

p-Aminophenyl piperidine, which may be compared with *p*-aminodimethyl aniline, reacts in many cases in a similar way to this compound. When oxidised with a primary, secondary, or tertiary amine, *indamines*, varying from blue to green, are produced. Oxidised in the presence of meta-diamines, compounds may be precipitated by means of zinc chloride which dye cotton blue.

With phenol, when oxidised with the theoretical quantity of potassium ferricyanide, a blue indophenol is obtained. With naphthols violet colours result. Other colours are also described by Lellmann and Geller (Ber. 1888, 2287).

Literature.—Anderson, Trans. Roy. Soc. Edin. 16, 463; 20, 247; 21, 219; 21, 571; Annalen, 70, 32; 84, 44; 94, 358; 105, 335; Weidel, Sitz. Ber. 79, 837; 80, 443; 80, 821; 81, 512; 90, 972; Ciamician, Ber. 1904, 4200–4255; Bamberger, Ber. 1891, 1758; and in general the papers of the following: Ciamician, Dennstedt, Hoogewerff and van Dorp, Liebermann, Oechsner de Coninck, and Weidel.

BONE PHOSPHATES *v.* FERTILISERS.

BOOKUM or **SAPPAN WOOD.** An Indian wood, the product of *Cæsalpinia Sappan* (Linn.). Used in dyeing reds.

BOOMAH NUTS. The fruit of *Pycnocoma macrophylla* (Benth.), belonging to the Euphorbiaceæ. Used in tanning (Holmes, Pharm. J. [3] 8, 363).

BORACIC or **BORIC ACID** *v.* BORON.

BORACITE. Borate and chloride of magnesium, $6MgO\cdot MgCl_2,8B_2O_3$, forming small, bright, sharply-developed cubic crystals of tetrahedral symmetry, in which the cube faces usually predominate. The crystals are interesting on account of their strong pyro-electrical characters, and the optical anomalies which they exhibit. Each cubic crystal is built up of twelve rhombic pyramids, the bases of which coincide with the twelve faces of the rhombic-dodecahedron and the apices meeting in the centre of the group. At a temperature of 265° the birefringence and twin-lamellæ disappear and the crystal is then truly cubic. This affords a good example of an enantiotropic change in state, the cubic modification being stable only above this temperature. The crystals usually occur embedded in gypsum, and are bounded on all sides by bright facets. Sp.gr. 2·9–3·0, H 7 (as high as that of quartz). They are found in considerable numbers at Luneburg, in Hanover, and at Stassfurt, and elsewhere in the Prussian salt-deposits. A massive earthy variety, known as 'stassfurthite,' occurs as nodules at Stassfurt in quantities sufficiently large for collecting for commercial purposes. J. L. S.

BORAL *v.* SYNTHETIC DRUGS.

BORATES *v.* BORON.

BORAX. As a mineral, borax ($Na_2B_4O_7,10H_2O$) is found as an efflorescence and as monoclinic crystals, sometimes of considerable size, on the shores of the salt lakes of Tibet and California. In San Bernardino and Lake counties in California there are several places known as 'Borax Lake'; but most of the borates commercially mined in this region belong to other species (ulexite, colemanite, &c.). The Tibetan deposits extend from the lake-plain of Pugha in the west to the lakes of Tongri Nur in the east, and formerly, since very early times, much crude material was exported under the name of tincal (*v.* Boron.) L. J. S.

BORDEAUX *v.* AZO- COLOURING MATTERS. Lambert (Zeitsch. anal. Chem. 22, 46) detects this dye in wines by precipitating with basic lead acetate, and extracting the precipitate with alcohol; the red solution thus obtained is turned yellow by alkalis. Wool heated with the wine withdraws its colouring matters.

Bellier (J. Pharm. Chim. [5] 14, 7) describes a method of determining quantitatively the amount of this dye in wines.

BORDEAUX MIXTURE *v.* PLANT SPRAYS.

BORNEO CAMPHOR *v.* CAMPHORS.

BORNEOL *v.* CAMPHORS; TERPENES.

BORNEO TALLOW is a generic term for a large variety of fats obtained from the kernels of a number of plants belonging to the *Dipterocarpus* family, such as *Shorea stenoptera* (Burck.), *Shorea aptera* (Burck.), *Hopea aspera* (de Verise), *Pentacme siamensis* (Kurz), all of which are indigenous to the Sunda Islands, Indo-China, and the Malay States. All the fats derived from these trees are also in commerce known under the native name of Minjak Tangkawang (Tangkawang Fat). Minjak Tangkawang represents a mixture of at least six fats, obtained from six varieties of trees known to the natives as Tangkawang toengkoel, T. rambei, T. lagar (these trees have a diameter of more than 3 ft.), T. goentjang (growing in swampy regions, and reaching a height of 22 ft., whilst the diameter of the trunk rarely exceeds 6 inches), T. madjan, T. terindak. The trees fruit only at irregular intervals, the nuts yielding, according to the species, from about 43 to 61 p.c. of fat.

The fat is prepared by the natives in a very crude manner. In the 'wet process' the fruits are placed in baskets, immersed in water, and left therein for from 30 to 40 days. After that time the shells are removed, the kernels are split into four parts, and these spread on boards, exposed to the sun to dry. The dried fruit is then pounded, boiled with water, and the liquid fat skimmed off and moulded in the internodes of bamboo stems; hence the commercial samples have a cylindrical shape. The 'dry process' consists in cutting the kernels into discs immediately after the fruit has been collected, drying the discs by exposure to the sun, and subsequently pressing. The fat obtained by the dry process yields the best product, which is largely used for edible purposes in the East. The kernels of the Shorea fruit (erroneously described in commerce as 'Illipé nuts,' *see* Bassia Oils), are shipped to Europe, where they are expressed, and the fat is used in the manufacture of candles and as a substitute for cacao butter. The commercial grades are described as 'large black Pontianac illipé nuts,' and 'large Pontianac or Sarawak illipé nuts without guarantee of colour.' 'Siak illipé nuts' are smaller, and yield a softer fat; they are the product of a species of *Palaquium* (N. O. *Sapotaceæ*).

In 1913, 8275 cwt. of illipé nuts, valued at £5954, were exported from Singapore, principally to Belgium, whilst small quantities were sent to the United States and to England (Bull. Imp. Inst. 1915, 23, 335).

Borneo tallow contains considerable quantities of stearic acid. Samples examined in the writer's laboratory contained as much as 66 p.c. of stearic acid. The fat melts at 29°–38°; and has iodine value 31–35·9; and saponification value, 190·4–194·5. The insoluble fatty acids have a high melting-point, viz. 53°–58°, and seem to consist of 66 p.c. of stearic acid and 34 p.c. of oleic acid. The fat separated from the kernels in Europe usually contains a high proportion of free fatty acids, the acid value of the product of Pontianac nuts being as high as 35.

The fats from *Shorea Ghysbertiana* and from *Isoperta bornensis* have been described as Enkabang fat and Teglam fat respectively (Brookes, Analyst, 1909, 206). J. L.

BORNESIT v. Glucosides.

BORNITE. A sulphide of copper and iron, of importance as an ore of copper (Cu 45–71 p.c.). On a freshly fractured surface the colour is dark bronze, but this quickly tarnishes to purple or deep reddish; hence the names purple copper-ore, variegated copper-ore (Buntkupfererz), erubescite, and the Cornish miner's name horse-flesh-ore. Further alteration produces a black sooty coating. The massive ore is always much intermingled with copper-pyrites, and even the rarely occurring cubic crystals usually contain a nucleus of copper-pyrites. The exact composition of the mineral has therefore long been doubtful; analyses by B. J. Harrington (1903) and E. T. Allen (1916) of carefully selected material gave the formula Cu_5FeS_4. This is the bornite of W. Haidinger (1845): bornite of F. S. Beudant (1832) is an obsolete synonym of tetradymite or telluric bismuth. L. J. S.

BORNYVAL. Pharmaceutical name for the *iso*valerianic ester of borneol $C_{10}H_{17}O{\cdot}C_5H_9O$, a limpid fluid smelling like valerian, insoluble in water, freely soluble in alcohol or ether; b.p. 255°–260°; sp gr. 0·951 at 20°, $[D]_{20}$ = 27° 40′.

BOROFORM. Trade name for a solution of formaldehyde in sodium glyceroborate.

BORO-GLYCERINE. An antiseptic, patented by Barff (D. R. P. 18108; Eng. Pat. 5906, 1884), prepared by heating 92 parts glycerol with 62 parts of boric acid at 200°. It is a yellowish, transparent substance, soluble in alcohol and in 40 parts of water. Used as a preservative for fruits and wines (J. Soc. Chem. Ind. 1, 244; 4, 362).

BORON. B. At. wt. 10·90 Smith and van Haagen. An element usually reckoned among the metalloids, although it presents analogies to the metals, and has been placed by Etard (Compt. rend. 91, 627) at the head of the vanadium group, intermediate between the places of phosphorus and carbon; is a triad in most of its known combinations, but is also capable of acting as a pentad (Michaelis and Becker, Ber. 13, 58). Never occurs free; usually as boric acid, and in several minerals, as *borax* or *tincal*, *boracite*, *hydroboracite*, *rhodizite*, *sassolite*, *borocalcite*, *boronatrocalcite*, and *botryolite*, and in small quantities in *schorl*, *datolite*, *tourmaline*, *apyrite*, and *axinite*. Minute quantities of boron are found in mineral waters; in sea-water; in plant ashes, and in animal tissues.

The element was first isolated by Gay-Lussac and Thénard in 1808, by heating boric oxide with potassium. According to Wöhler and Deville (Ann. Chim. Phys. [3] 52, 63), it may be obtained by mixing 60 grams of sodium in small pieces with 100 grams of powdered boric oxide in an iron crucible, covering the mixture with a layer of 30 grams ignited sodium chloride in fine powder, and heating the whole to redness. After the completion of the reaction, which is very violent, the mixture is stirred with an iron rod, until the sodium and sodium chloride are fused, and carefully poured into dilute hydrochloric acid, and the residue washed with water containing ammonium chloride (which salt is subsequently removed by alcohol) and dried. Boron can also be obtained by heating potassium borofluoride with potassium (Berzelius), or magnesium (Wöhler and Deville); by the electrolysis of fused boric oxide (Davy); by reducing boron trichloride by hydrogen (Dumas), or preferably with hydrogen in the high tension electric arc; by fusing borax with amorphous phosphorus (Dragendorff); by heating boric oxide with magnesium or calcium, and treating the residue with dilute hydrochloric acid. Boron may also be obtained by the dissociation of the nitride, or of magnesium boride at high temperatures.

Wöhler and Deville's method gives a product containing, in addition to boron, compounds of boron with sodium, iron, and hydrogen, and boron nitride. The best method is that of Moissan, as modified by Weintraub (J. Ind. Eng. Chem. 1911, 3, 299; 1913, 5, 106). Pure and dry boric oxide is intimately mixed with as much magnesium filings as will suffice to reduce one-third of it. The mixture is placed in an earthenware crucible in a furnace at a bright-red heat, when the reaction proceeds at once rather violently. Heating is continued for ten minutes and the mass allowed to cool. The middle portion of the mass, which is of a reddish colour, is mechanically separated from the surrounding black portion as completely as possible, and boiled with a large excess of dilute hydrochloric acid which removes the boric acid and borides of magnesium. The magnesium borate is removed by repeated boiling with strong hydrochloric acid; and the silica (resulting from the disintegration of the crucible) by heating the residue in a platinum vessel with hydrofluoric acid. The residue is washed by decantation with water and dried. It is then approximately pure, but still contains a small quantity of a magnesium boride which cannot be got rid of except by fusing the product with about fifty times its weight of boric oxide, and repeating the above operations.

The product when heated *in vacuo*, at a sufficiently high temperature, or when heated to bright redness in hydrogen with excess of magnesium or sodium, and extracted successively with water, hydrochloric acid and hot dilute nitric acid yields pure boron (Ray. Chem. Soc. Trans 1914, 105, 2162).

Boron has been produced by Weston and Ellis (Trans. Faraday Soc. 1907, 170) by the action of aluminium powder on boric oxide. If 2 mols. of boric oxide to 2 atoms of aluminium are used, the chief product is boron, but with a smaller proportion of boric oxide aluminium boride is produced to a large extent.

Boron may be prepared electrolytically as follows: A fused metallic borate is electrolysed between carbon poles separated so as to prevent the boron floating to the cathode. By the use of a high-current density at the anode sufficient heat is generated to effect the reduction of the boric oxide which collects there (U.S. Pat. 785962).

Commercial boron is purified by grinding the product obtained by heating boric oxide and magnesium with hydrochloric acid, and quickly pouring off the upper liquid. This contains matter in suspension which holds a higher proportion of impurities than does the residue at the bottom. This process of 'fractional decantation' is repeated several times. The residual boron, which may still contain boron hydride, magnesium boride, boric oxide, and a borate, is compressed into a thick stick or cake, and heated to 1200° in a vacuum electric furnace, which either volatilises or dissociates all these impurities. The pure boron is then melted down in the arc in a current of inert gas, preferably hydrogen. The resulting boron is a dense solid substance which conducts electricity and is completely fusible without apparent volatilisation (British Thomson-Houston Co., Eng. Pat. 1197, 1907). Colloidal solutions of boron have been prepared by Gutbier (Kolloid. Zeitsch. 1913, 13, 137).

The amorphous boron described by Moissan and others as a chestnut-coloured powder of sp.gr. 2·45 always contains oxygen, and appears to be a solution of a lower oxide of boron and of magnesium oxide in boron in the superfused liquid state; it is tasteless, odourless, staining the fingers strongly; becomes denser on being heated in a vacuum or in gases which have no action upon it; not oxidised at ordinary temperatures in either air or oxygen; heated in air, it burns with a reddish light, forming B_2O_3 and BN; burns with dazzling brightness in oxygen, forming B_2O_3. Boiling water has no action on it, but it is readily oxidised by strong nitric acid in the cold, and by sulphuric acid when heated. When heated to redness with the alkaline salts of oxyacids, yields an alkaline borate, the formation being frequently attended with incandescence, and in the case of nitre with explosion. Heated with potash it forms potassium borate with liberation of hydrogen, and reduces the chlorides of lead, gold, mercury, and silver, and sulphides of lead, chloride or sulphide of boron being formed (Wohler and Deville, *l.c.*; and Annalen, 105, 72). Heated in nitrogen, it forms white boron nitride. It decomposes nitric oxide at a red heat, burning brilliantly and forming boric oxide and nitride, but apparently has no action on nitrous oxide. (*Cf.* Kroll, Zeitsch. anorg. Chem. 1918, 102, 1.)

Crystalline boron—the only pure form of boron—is a black solid of sp.gr. 2·34, almost as hard as diamond, and only inferior to it in toughness and strength. Melts at about 2200°, and has a sensible vapour tension at 1600°. Rapidly increases in electrical conductivity when heated. It may be obtained by placing 3 parts of aluminium with 10 parts of fused boric acid in a gas-carbon crucible filled up with ignited charcoal and placed inside another crucible of graphite which is heated to 1500°, for five hours. The aluminium is removed from the resulting mass by means of fairly strong soda, and the residue is then boiled out with hydrochloric and hydrofluoric acids. The residue contains some alumina which is separated mechanically as far as possible, and completely by glacial phosphoric acid. Crystals may also be obtained by heating 2 parts of fused and powdered borax with 1 part of magnesium. A commercial process has been patented by Kühn (Chem. Zentr. 1904, i. 64). Boron compounds are mixed with sulphur and aluminium, and the mixture, which burns, ignited. Crystals of boron are found in the resulting mass, and are separated from it by extraction with water, which decomposes the aluminium sulphide, forming aluminium hydroxide and H_2S, and leaving the crystals of boron.

It is only oxidised with very great difficulty in oxygen, and in air no change takes place even at 2000°. Molten potash or lead chromate oxidises it with incandescence, but fused potassium nitrate does not affect it. 'Boron diamonds' of the composition $B_{48}C_2Al_3$ (Hampe) ($C_2Al_3B_{44}$, Biltz) may be obtained by strongly heating a mixture of boron trioxide, sulphur, aluminium and soot. The fused mass gives a mixture of yellow transparent quadratic crystals mixed with black opaque crystals of AlB_{12}, which can be separated by fractional flotation in a mixture of methylene iodide and benzene, the yellow quadratic crystals being slightly heavier than the others. They are not attacked by hot strong hydrochloric or sulphuric acids, or by a solution of chromic anhydride in strong sulphuric acid (Biltz., Ber. 1910, 43, 297).

Boron may be introduced into steel, and the properties of the boron steel so obtained have been studied by Osmond (Compt. rend. 110, 242, and 346), by Moissan and Charpy (*ibid.* 120, 130), by L. Guillet (*ibid.* 144, 1049), and by Hannessen (Zeitsch. anorg. Chem. 1914, 89, 257). Boron steels are obtained either by heating amorphous boron with reduced iron in a current of hydrogen, or by adding crystalline boron to the molten metal. On hardening by heating to a known temperature and quenching, boron steel behaves like a high-grade hard carbon steel as regards increase in tensile strength, whilst the diminution in extension is not so great. The hardness of boron steel is not much affected by heating and quenching. The special effect of boron appears to be to communicate to the steel a high tensile strength rather than actual hardness when the metal is heated and quenched.

Boron rapidly reduces manganese oxides in the electric furnace. With excess of oxide products containing up to 97 p.c. manganese may be obtained which are soft enough to be filed. With excess of boron, harder, granular substances result, containing up to 20 p.c. boron. From these a definite boride MnB may be isolated. It is a crystalline metallic powder attacked by halogens and oxygen at high temperatures, and by alkali hydroxides and carbonates at a red heat. Water or steam slowly decomposes it with evolution of hydrogen (Binet du Jassonneix, Compt. rend. 139, 1209). The same author has obtained very similar results with molybdenum dioxide and boron (Compt. rend. 143, 169); and has also prepared two definite borides of chromium Cr_3B_2 and CrB, by fusing together chromium and boron. They are very stable towards reagents, especially the former, but are decomposed by fused alkalis, and by chlorine at a red heat. They are soluble in hydrofluoric, hydrochloric, and concentrated sulphuric acids (Compt. rend. 143, 1149). The same author has also prepared Ni_2B, NiB_2, Co_2B, and CoB_2 (Compt. rend. 145, 240); and borides of zirconium, chromium, tungsten, and molybdenum have been prepared by Tucker and Moody (Chem. Soc. Proc. 1901, 129); and borides of vanadium, uranium and titanium by Wedekind, Horst and Jochem (Ber. 1913, 46, 1198).

COMPOUNDS OF BORON WITH NON METALLIC ELEMENTS.

Boron hydrides are formed by dissolving magnesium boride in hydrochloric acid, or more easily by dissolving commercial ferroboron in dilute sulphuric acid. Spontaneously inflammable. Boron hydrides admixed with hydrogen are evolved, and an insoluble residue formed. The gases have a characteristic smell, and decompose a moderately concentrated silver nitrate solution, forming a blackish-brown precipitate with metallic lustre. They burn with a green flame and form a mirror when passed through a red-hot glass tube (Hoffmann, Chem. Zeit. 1911, 35, 265).

Four unstable hydrides have been isolated, B_2H_6, B_4H_{10}, B_6H_{12}, and a solid hydride $B_{10}H_{14}$. Boron hydride, B_4H_{10}, is a colourless liquid, b.p. 16°–17°/760 mm.; m.p. *ca.* −112°, of a peculiar and most disagreeable odour. A few bubbles of the gas affect respiration and cause headache. It is a very unstable substance, decomposing at the ordinary temperature after a few hours, especially under the influence of ultra-violet light, and quicker at higher temperatures, giving rise to B_2H_6. It is similarly decomposed by electric sparks. It takes fire spontaneously in the air or in oxygen, burning with a green flame. Water and dilute hydrochloric acid decompose it, and it is oxidised by concentrated nitric acid with explosive violence. It is rapidly absorbed by aqueous sodium hydroxide, the solution slowly evolving hydrogen. Ammonia gives a solid light brown substance, insoluble in water, whilst alcohol decomposes the hydride with evolution of hydrogen. The solution in benzene is very stable towards oxygen.

The hydride B_6H_{12} is a colourless liquid, b.p. 10°/15 mm. *ca.* 100°/760 mm., possessing a highly disagreeable odour and taking fire spontaneously in the air. It is more sensitive towards water and moisture than the hydride B_4H_{10}. With aqueous alkalis, hydrogen is immediately evolved (Stock and Massenez, Ber. 1912, 45, 3568).

B_2H_6 is a colourless gas possessing a characteristic, repulsive odour, resembling that of the hydride B_4H_{10}. B.p. −87° to −88°/760 mm., m.p. −169°. It is more stable than B_4H_{10}, but decomposes slowly at ordinary temperatures. It only takes fire in the air when mixed with other boron hydrides. With alkalis, it reacts similarly to B_4H_{10}; with sodium hydroxide it gives solutions containing hypoborates.

The formula B_2H_6 shows that boron must be at least quadrivalent and not tervalent as a maximum, as it should be according to its position in the periodic system (Stock and Friederici, Ber. 1913, 46, 1959).

The solid hydride $B_{10}H_{14}$ obtained by heating the other hydrides is a colourless substance with a penetrating peculiar odour, dissimilar to that of the gaseous hydrides. It sublimes in a vacuum giving long needles, m.p. 99·5; D 0·94. Not attacked by water, even when boiling, soluble in alkaline hydroxide, giving intense yellow solutions (Stock, Friederici and Priess, Ber. 1913, 46, 3353).

All the hydrides when treated with caustic alkalis evolve hydrogen and form alkaline hypoborates: thus with potassium hydroxide, $B_4H_{10}+4KOH=4KOBH_3+H_2$. The solutions of the hypoborates thus formed are stable for hours at 0°, but on boiling they decompose rapidly. *Potassium hypoborate* $KOBH_3$ forms glistening, octahedral, colourless crystals which are stable in dry air. It is deliquescent, and its solutions gradually decompose at ordinary temperatures, evolving hydrogen and forming potassium borate. The aqueous solution is a strong reducing agent, giving with copper salts a precipitate of copper hydride, and with nickel salts black insoluble nickel boride, Ni_2B (Stock and Kuss, Ber. 1914, 47, 810. For action of halogens on the hydrides, *see* Stock, Kuss and Priess, Ber. 1914, 47, 3115).

Boramide $B(NH_2)_3$ is formed together with ammonium chloride by the action of ammonia on boron trichloride at a low temperature (Joannis, Compt. rend. 135, 1106).

Borimide $B_2(NH)_3$ is a spongy white mass insoluble in most solvents. On heating it begins to give off ammonia at 125°–130°, and is completely transformed into boron nitride at slightly higher temperatures. It is prepared by heating the compound of boron trisulphide and ammonia $B_2S_3,6NH_3$ for some time at 115°–120° in a current of hydrogen or dry ammonia (Stock and Blix, Ber 1901, 3039; and Joannis, Compt. rend 135, 1106).

Boron carbide B_6C forms exceedingly hard shining black crystals, which are capable of polishing diamonds. It may be obtained massive by fusing together boric oxide and carbon in an electric resistance furnace and cooling fairly rapidly (E. A. Sperry, U.S. Pat. 869114).

Shaped blocks of boron carbide are obtained by preparing the body of the block in pure carbon, embedding this in powdered carbide, and firing in an electric furnace (Bolling, Eng. Pat. 6693, 1905). Modifications of this process have also been patented (Additions (2) Sept. 30, 1904, to Fr. Pat. 353017).

Boron nitride BN is a white, amorphous, bulky powder discovered by Balmain in 1842. It is infusible, insoluble in water, and generally somewhat inert to reagents, but Stock and Blix (Ber. 1901, 3039) have described another modification which is chemically much more active. It may be obtained mixed with B_2O_3 by burning boron in air; or by the action of nitrogen on a mixture of boric anhydride and carbon heated to redness (Wöhler and Deville, Ann. Chem. Phys. [3] 52, 84). It may be prepared by the action of ammonium chloride vapour on a porous mass of calcium phosphate and borax or boric oxide heated to bright redness, afterwards extracting the cold mass with hydrochloric acid and water, and drying the residue of BN in a vacuum desiccator (Moeser and Eidmann, Ber. 1902, 535); or by allowing boron bromide to drop into liquid ammonia, and heating the precipitated mixture of boramide and borimide to 750° in a current of ammonia gas (Stock and Holle, Ber. 1908, 2095); or by heating boric acid and calcium cyanamide. A mixture of borocalcite CaB_4O_7 and carbon heated to 1850° and then to 1400°, affords a theoretical yield of boron nitride (Stähler and Elbert, Ber. 1913, 46, 2060). B_3N has been prepared by heating boric acid with magnesium nitride.

Boron sulphide B_2S_3 forms fine white needles of density about 1·55, which melt at 310°. It is volatile in hydrogen without decomposition (Moissan, Compt. rend. 115, 203). It may be prepared by heating together sulphur and amorphous boron (Wöhler and Deville); or, better, by heating ferroboron in a stream of dry hydrogen sulphide at 400°, and purifying the resulting product by dissolving out the sulphur with carbon disulphide (Hofmann, Zeit. angew. Chem. 1906, 1302). Combines with hydrogen sulphide to form *thiometaboric* acid $H_2B_2S_4$. Is decomposed by carbon dioxide.

Boron trifluoride BF_3. Amorphous boron unites with fluorine at the ordinary temperature. It is a gas at ordinary temperatures, and may be prepared by heating a mixture of boron trioxide and calcium fluoride with sulphuric acid, or a mixture of potassium borofluoride and boron sesquioxide with sulphuric acid. It may be liquefied and solidified by cold and pressure: melts at −127° and boils at −101°. It is rapidly decomposed by water, forming hydrofluoboric and boric acids.

Boron trichloride BCl_3 is a colourless, very mobile, refractive liquid which fumes in the air. Sp.gr. 1·4338 at 0°; m.p. −107°, b.p. 12·5°. It is decomposed by water with formation of hydrochloric and boric acids. It is prepared by passing dry chlorine over amorphous boron, and collecting the vapours in a U-tube immersed in a freezing mixture. The product is purified by shaking with mercury to remove chlorine, and by fractionation. It may also be prepared by heating boron sesquioxide with phosphorus pentachloride.

Boron tribromide BBr_3 resembles the chloride in physical properties. It is prepared in the same way, substituting bromine for chlorine, or by treating a red-hot mixture of carbon and boric oxide with bromine vapour. M.p. −46°; b.p. 90·5°; sp.gr. 2·65 at 0°.

Boron tri-iodide BI_3 may be obtained by acting on heated amorphous boron with iodine or hydriodic acid, or by treating the vapour of the trichloride with hydrogen iodide. It crystallises in colourless nacreous plates and is readily acted upon by light. M.p. 43°; b.p. 210°. Soluble in carbon disulphide, benzene, and other organic solvents. Burns when heated in oxygen, and is decomposed when warmed with sulphur or phosphorus.

Boric oxide B_2O_3 may be obtained by burning boron in oxygen, or, more easily, by strongly heating boric acid, when it melts at 577° to a viscid mass, cooling to a colourless brittle glass of sp.gr. 1·88. May be vaporised *in vacuo*, and is capable of expelling carbonic, nitric, and sulphuric acids from their salts at a red heat. Soluble in water, forming boric acid. For velocity of hydration of boric oxide to metaboric acid and orthoboric acid, see Myers, Chem. Soc. Trans. 1917, 111, 172.

A blue glass, 'boron-ultramarine,' of colour varying with the duration and intensity of heating, and with the proportions of the ingredients, is made from sodium sulphide and boric anhydride. It is stable in air and only slightly soluble in water (J. Hoffmann, Zeitsch. angew. Chem. 1906, 1089).

Tetraboron trioxide B_4O_3, *boron dioxide* B_2O_2, and *tetraboron pentoxide* B_4O_5 are also known.

Boric or **Boracic acid.** *Sal sedativum Hombergii*, *Sal narcoticum vitrioli.* Boric oxide forms three hydrates:

Orthoboric acid $B_2O_3{\cdot}3H_2O=H_3BO_3$.
Metaboric acid $B_2O_3{\cdot}H_2O=H_2B_2O_4$.
Pyroboric acid $2B_2O_3{\cdot}H_2O=H_2B_4O_7$.

Ray (Chem. Soc. Trans. 1918, 803) has described the mode of formation of a potassium borate $K_2B_4O_6$, and hence the existence of an acid $H_2B_4O_6$.

Boric acid appears to be a dibasic acid, and most of its salts may be regarded as derived from metaboric or pyroboric acid. Both these are so-called 'weak' acids. Their salts, when soluble, have usually an alkaline reaction, even when containing excess of boric acid, and are decomposed even by carbonic acid.

Boric acid is found free in nature in many volcanic districts. In Central Italy it is produced on a large scale in the territories of four communes: Pomerance, Massa Marittima, Castel Nuovo di Val di Cecina, Montieri, all in the province of Tuscany, the nearest shipping point being Leghorn, to which place it is brought by railroad from Volterra. It also occurs in the extinct crater of a volcano on one of the Lipari Islands, and in the crater of Stromboli, an active volcano on another island of the same group, near Sicily. Volcanic emanations containing boric acid occur in Nevada, in California, and Nova Scotia. It exists in solution in the mineral waters of Wiesbaden, Aachen, and Krankenlied, in Germany; in the mud volcanoes of the Colorado Desert, in San Diego county, California; in the water of several mineral springs in Tehama county, California. In smaller quantities it exists in sea water and in the ash of many plants.

Sassolite, or Tuscan boric acid, is never produced in the pure state, but is always associated with impurities, both soluble and insoluble. It differs considerably in quality, some parcels containing 89 p.c. of crystallised acid, while others yield only 75 p.c. The following analyses show its general composition:—

Analyses of crude Tuscan boric acid.

Boric acid B_2O_3 . . .	47·95	44·04
Water { combined . . .	37·00	33·98
Water { hygroscopic . .	0·73	2·80
Ammonium sulphate $(NH_4)_2SO_4$	5·67	10·62
Sulphate of alumina and iron	0·13	0·20
Calcium sulphate . . .	trace	1·20
Magnesium sulphate . .	6·91	4·03
Sodium sulphate . . .	0·07	1·10
Sodium chloride . . .	0·23	0·32
Sand	0·42	0·80
Sulphur	—	trace
Organic matter . . .	0·89	0·91
	100·00	100·00

An analysis of an average sample taken from 5000 tons shows it to be composed as follows :—

Crystallised boric acid $B_2O_3,2H_2O$	83·5
Hygroscopic water	1·4
Ammonium sulphate	5·3
Magnesium sulphate	7·5
Iron and alumina	0·3
Sand, organic matter, &c.	2·0
	100·0

Boric acid occurs on the West Coast of South America, principally in the form of boronatrocalcite (*ulexite*, or *hayesine*), and is found throughout the province of Atacama and in portions of Chile. Ascotan and Maricunga, to the north of Copiapo, are the places which have proved most successful commercially. The crude material, known as *tiza*, occurs in both places in lagoons or troughs; these, instead of being entirely filled with common salt, as is usually the case in the desert, contain zones or layers of boronatrocalcite, alternating with layers of salt and salty earth. The lagoons of Maricunga are estimated to cover 3,000,000 sq. metres. The raw material contains on the average about 25 p.c. of boric acid, but by washing and calcination it may be raised to 55 or 60 p.c. The roughly purified boronatrocalcite is shipped to England and Germany.

A borate of lime (*rhodizite*) is imported from the West Coast of Africa.

Pure orthoboric acid is easily obtained by treating a solution of 3 parts borax in 12 parts hot water with 1 part sulphuric acid. On cooling, boric acid separates out; it is recrystallised from hot water, dried and fused to expel traces of sulphuric acid, and again recrystallised from water. It forms white, translucent, monoclinic laminæ (Kenngott), which have a mother-of-pearl lustre and are unctuous to the touch. Sp.gr. 1·434 at 15°.

Boric acid evaporates freely in a current of steam. The loss sustained by evaporating an aqueous solution is 0·28 p.c. of the water evaporated, equal to 2 8 lbs. for every 100 gallons. (*Cf.* Nasini and Ageno Atti. R. Accad. dei Lincei, 1912, 21, ii. 125.)

The solubility of boric acid in water has been determined by Ditto (Compt. rend. 85, 1069), but his results are probably low. Herz and Knoch find considerably higher values at 13°, 20°, 25°, and 26°. The figures of Brandes and Firnhaber (Arch. Pharm. 7, 50) also differ. The results obtained by Nasini and Ageno (Zeitsch. physikal. Chem. 1909, 69, 482) are quoted below :

Temperature	Grams of H_3BO_3 per 100-gram solution.	Temperature	Grams of H_3BO_3 per 100-gram solution
0°	2·59	60°	12·90
12·2°	3·69	69·5°	15 58
21°	4·90	80°	19·11
31°	6·44	90°	23·30
40°	8·02	99·5°	28·10
50°	10·35		

Cf. Nasini and Ageno (Gazzetta, 1911, 41, i. 141).

The solubility of orthoboric acid in water is lessened (not, as stated in various places, increased) by the presence of hydrochloric acid (Herz, Chem. Zentr. 1903, i. 312) and of sulphuric, nitric, and acetic acids; but tartaric and oxalic acids have the opposite effect (*ibid.* 755). Boric acid is soluble in alcohol, glacial acetic acid, and volatile oils. A cold saturated aqueous solution colours litmus [illegible] wine-red; a hot saturated solution gives a bright-red colour.

Crystallised boric acid, heated to 100°, is converted into $H_2B_2O_4$ (Schaffgotsch, J. 1859 71), and into $H_2B_4O_7$ at 160° (Merz, J. pr. Chem 99, 179; Ebelmen and Bouquet, Ann. Chim Phys. [3] 17, 63). At a stronger heat the acid froths up, parting with its water and forming boric anhydride as a fused viscid mass, solidifying to a fissured glass on cooling. For the action of boric acid on sodium chloride on heating, *see* Levi and Castellani (Gazz. chim. ital. 1910, 40, i 138); Levi and Garavini (*ibid.* 1911, 41, i. 756).

Boric acid and its salts are extensively used in medicine as an antiseptic; and as a food preservative they are also very widely employed. They are also employed for glazing porcelain and earthenware, in the preparation of glass and certain pigments, in the manufacture of cosmetics, soaps, in the linings of safes, in the glazing of paper, for dressing leather, as a flux, by laundresses, and for soaking the wicks of stearin candles.

The effect of boric acid in glazes is to increase their hardness and their fusibility, and to modify the coefficient of expansion. A small amount of boric acid lowers the expansion, whilst a large quantity produces an increase. This effect is explained by Grenet (Compt. rend. 123, 801) to be due to the fact that when the proportion of bases to boric acid is high, devitrification occurs, whilst when the boric acid is the more important constituent, the coefficient of expansion tends to approximate to that of boric acid itself, which is higher than that of any glass.

It has also been proposed to use boric acid in the preparation of nitric acid from Chile saltpetre, so as to obtain borax as a by-product.

Industrial extraction of boric acid. The occurrence of the *sal sedativum* of Homberg in the water of the Tuscan lagoons appears to have been first noticed in 1777 by Höfer, a Florentine apothecary, and its extraction was begun about 1815, and to-day a large part of the boric acid of commerce is derived from the lagoons near Monte Rotondo, Lago Zolforeo, Sasso, and Larderello, in the Maremma of Tuscany, inclosing both natural and artificial vents. The *soffioni* or jets of steam, which often rise in thick columns to a considerable height, contain only traces of boric acid, but when these are condensed in the water of the lagoons this becomes gradually charged with the acid which is obtained from the solution by evaporation.

To obtain the boric acid, the soffioni are surrounded by basins of rough masonry, several of which are arranged in steps, one above the other, in such manner that the contents of each basin can be led by gravitation into the basin below. Fresh water from a neighbouring spring is conducted into the uppermost basin, whilst the gases and vapours of the fumaroles rise through the water from beneath, occasionally with such violence as to eject the water to a height of several feet. After twenty-four hours the water in the first basin, which is generally muddy, is allowed to pass into the second basin, the first being recharged with fresh water. After another twenty-four hours the second basin is discharged into the third and the first into the second, the second and following basins being also built round soffioni. After having passed through four or five of these basins, the solution is passed into rectangular reservoirs in which the suspended matter is deposited on standing. From these it passes into a series of leaden evaporating pans, placed in couples one above the other in the form of a terrace. These pans are heated by the gases and vapours of soffioni which, on account of their situation, are otherwise useless—by a method first adopted by Count Lardarel in 1815. The evaporating pans are square, about 1 foot deep and 9 feet square, and are supported on wooden beams. The solution is heated in these for twenty-four hours until it has attained a density of 1·017, when it is decanted into a second series of pans, where, after another twenty-four hours, it attains a density of 1·034, and is finally decanted into the last four pans, where it is evaporated to a specific gravity of 1·07.

The temperature gradually increases, being in the first pans about 60° to 70°, in the following pans about 75°, and in the last as high as 80°.

In all these pans a precipitation of gypsum takes place, which requires to be removed from time to time. When the solution in the last pans has attained a density of 1·07, it is run through funnels into the crystallising vats, consisting of wooden tubs lined with lead. After twenty-four hours the crystallisation is complete, the mother liquor is then decanted off and added to the evaporating pans a few hours before the completion of the concentration. The crystals are drained in baskets placed under the crystallising vats for twenty-four hours, and are spread out on the bottom of a large drying oven, which is likewise heated by the vapour from the soffioni. The layer of crystals, which is two or three inches thick, is stirred at intervals to assist the drying. This is complete in twenty-four hours. An improved form of evaporating apparatus consists in decanting the solution in the reservoirs from which the suspended matter has deposited into a pan, and thence running it into a slightly inclined trough made of sheet lead with the edges turned upwards. The trough has an undulatory form, is supported on wooden sleepers, and heated by the soffioni vapours. The solution of boric acid, after passing through this heated trough, becomes so concentrated as to be ready for crystallisation.

Artificial soffioni have been bored to a depth of 200 feet in the vicinity of the Monte Rotondo. The chief works are at Monte Cerboli, Larderello, San Federigo, Castel Nuovo, Sasso, Monte Rotondo, Lustignano, Serranzano, Lago, and San Eduardo, each of which has from 8 to 35 *lagoni*, 100 to 200 feet in diameter (Payen, Ind. Chem. transl. by Paul).

The boric acid thus obtained is far from pure. Analyses of different samples by Payen, Vohl, and Wittstein show that it contains from 74 to 80 p.c. crystallised boric acid, from 4·5 to 7 p.c. of hygroscopic water, ammonium and magnesium sulphates, 8–14 p.c., together with gypsum, clay, sand, sulphur, organic matter, and free acids and ammonia.

The origin of the boric acid in the soffioni is not understood. Dumas suggested that it is formed by the decomposition by means of water of a bed of boron sulphide formed at some depth below the surface. Bolley (Annalen, 68, 122) supposed that it is produced by the action of a hot solution of ammonium chloride upon the borates contained in the earth. According to Warington (Chem. Gazette, 1854, 419), Wöhler and Deville (Annalen, 105, 69), and Popp (Annalen, Suppl. 8, 1), its formation is probably due to the action of water upon boron nitride.

Dieulafait has found boric acid in regions where there are no visible manifestations of volcanic action, and concludes that it is of aqueous origin, and derived from the waters of ancient seas (Compt. rend. 100, 1017, and 1240).

Of late years the importation of boracite from South America and colemanite from California, and also some Persian ores, has had a considerable effect on the Italian industry. Besides the obvious method of separating the boric acid from these ores by acidification and crystallisation, other processes are used for its extraction.

One process consists in grinding the borate of lime or ulexite to an impalpable powder and treating it with sulphurous acid.

A large wrought-iron tank, circular in shape and egg-ended, is lined with stout sheet lead; it is provided with a cover and still head, mechanical agitator, and steam pipes. It is first of all charged about half full with water or weak liquor from a previous operation. The liquor is then boiled, and the powdered borate fed in by means of an Archimedean screw.

Sulphur is then burnt in an adjoining furnace, and the sulphurous gas is injected by means of a peculiarly constructed lead injector into the boiling liquor. A special type of sulphur burner for this process is patented by the American Borax Co. (U.S. Pat. 809550, 1906). The gas is wholly absorbed by the calcium borate, which itself is slightly soluble in water, boric acid and calcium sulphite being formed. The steam arising from the operation, containing boric acid vapours, passes from the still head through a condenser in order to prevent any loss that would occur. When the operation is complete, the steam and gas are shut off, and the contents of the pan allowed to settle, which occupies about ten hours. The clear boric acid liquor is then run either into vats made from white sugar pine, or of ordinary wood lead-lined, where the boric acid crystallises out. The mother liquors are then drawn off, to be used over again if not too highly impregnated with foreign salts, or still further treated for the recovery of the calcium sulphite and the slight percentage of boric acid they contain.

Bigot (J. Soc. Chem. Ind. 1899, 830) obtains it by heating together borate of calcium and ammonium sulphate in a closed vessel. The ammonia driven off is condensed and collected, and the boric acid obtained by extraction of the residue.

Another method is to treat boracite with sodium bisulphate, a by-product in nitric acid manufacture. The two are dissolved in theoretical quantities in water to a density of 15° B. at 100°. The solution is filtered and concentrated to 30° B. On cooling, the boric acid crystallises out and very pure sodium sulphate is obtained by concentration of the mother liquors (Heidlberg, Chem. Zeit. 1907, 31, Rep. 48).

Chenal Douilhet & Co. (D. R. P. 110421, 1899) produce boric acid by taking advantage of the fact that when a borate is boiled with ammonium chloride, ammonia and boric acid are produced. If the concentration is too high, there is a tendency to recombination; the boric acid is therefore removed frequently by crystallisation from portions of the liquid, the mother liquors being returned to the main volume. By this process it is claimed that 98–99 p.c. of the boric acid in combination is recovered.

In another process chlorine is passed into water at 70° containing finely powdered calcium borate in suspension. Calcium chloride and chlorate and boric acid are produced. The boric acid is removed by cooling, and the mother liquors used again until sufficiently concentrated for convenient extraction of the chlorate (G. C Moore, Eng. Pat. 20384, 1899).

METALLIC BORATES.

Borates are obtained by the action of boric acid on metallic oxides or their salts, in either the dry or wet way.

In solution boric acid is a very weak acid, being expelled by almost all acids from its combinations, partially so even by carbonic and hydrosulphuric acids. A boiling concentrated solution, however, decomposes carbonates and soluble sulphides and manganese sulphide.

In the dry way, at high temperatures, it is capable of decomposing the salts of all more volatile acids.

Alkaline borates are soluble in water, but are precipitated by alcohol. The remaining borates are insoluble, or very sparingly soluble in water. The soluble borates produce precipitates in solutions of salts of calcium, barium strontium, nickel, and cobalt, and of ferric salts which are readily soluble in ammonium chloride.

Anhydrous borates are produced by fusing together, in a special furnace at 1350°–1400° for three hours, boric oxide with the necessary quantity of oxide, carbonate, or nitrate of the metal. With large excess of boric acid, lithium, potassium, sodium, rubidium, cæsium, thallium, and silver produce clear fusions which either crystallise or leave clear glasses on cooling. Cuprous oxide, and oxides of lead, bismuth, antimony, arsenic, titanium, molybdenum, and tungsten produce clear fusions at the high temperatures which form emulsions on cooling. The oxides of calcium, strontium, barium, magnesium, zinc, cadmium, manganese, iron, cobalt, and nickel, do not give homogeneous fusions, but separate into two layers (W. Guertler, J. Soc. Chem. Ind. 1908, [illegible]58).

Borates have also been prepared electrolytically by Levi and Castellani by electrolysing boric acid and an alkaline earth chloride in a special type of divided cell (J. Soc. Chem. Ind. 1909, 248).

Ammonium borates. *Laderellite*

$$(NH_4)_2B_{10}O_{16},5H_2O$$

occurs in the Tuscan lagoons in small crystalline rhomboidal plates (D'Achiardi, Chem. Soc. Abstr. 1900, 600). Atterberg (Zeitsch. anorg. Chem. 1906, 48, 367) distinguishes a *diborate* $(NH_4)_2B_4O_7,5H_2O$, crystallising in tetragonal pyramids, besides the *pentaborate*

$$(NH_4)_2O,5B_2O_3.3H_2O,$$

crystallising in rhombic double pyramids previously prepared by Rammelsberg. *Cf.* Sborgi (Atti R. Accad. dei Lincei, 1912, 21, ii. 855; 1913, 22, i. 90).

Barium borates. The interaction of barium hydroxide and boric acid in aqueous solution has been studied by Sborgi (Atti R. Accad. dei Lincei, 1914, 23, i 530, 717, 854). The only stable compounds which appear to exist are the triborates $(BaO,3B_2O_3, + H_2O)$ and the metaborate $(BaO.B_2O_3 + H_2O)$.

Calcium borates $Ca_2B_6O_{11}$. There are three varieties of calcium borate, which correspond to the three varieties of calcium carbonate, calc spar, marble, and chalk—viz. *boracite* or *pandermite*, *colemanite*, and *pricite*—each found in different parts of the world in large quantities, and of a well-defined and constant composition. Meyerhoffer and van 't Hoff (Annalen, 351, 100), [illegible] attempting to prepare compounds of similar composition artificially, have obtained several other calcium borates. These authors assign different compositions to colemanite and pandermite. *Boracite*, in outward appearance, closely resembles a snow-white, fine-grained marble; *colemanite* is of a crystalline nature like calc spar, or Iceland spar, and has been termed *borate spar*; *pricite*, or *bechilite*, is a very fine, white, soft, chalky mineral of a cohesive nature, easily rubbed to powder, and resembling chalk. Chemically speaking, they are all hydrated calcium borates, differing only in their composition in respect to the water of combination, their composition being given in table below.

—	$Ca_2B_6O_{11},3Aq.$	$Ca_2B_6O_{11},4Aq.$	$Ca_2B_6O_{11},5Aq.$	$Ca_2B_6O_{11},6Aq.$
Boric acid B_2O_3	55·8	53·3	50·9	48·8
Lime CaO	30·0	28·4	27·2	26·1
Water H_2O	14·2	18·3	21·9	25·1
	100·0	100·0	100·0	100·0

Cf. Sborgi (Atti R. Accad. dei Lincei, 1913, 22, i. 639, 715).

Boracite has been extensively mined at Sultan-Chairi, in the district of the Villayet of Broussa in Asia Minor, forty-five miles from Panderma, a port on the Sea of Marmora; the principal deposits, as far as yet known, exist near the Tschataldga Mountain, in long. 28° 2′ east of Greenwich and lat. 40° north. The Susurlu river runs from the Tschataldga Mountain to the Sea of Marmora: it is partly navigated to a point called Mohalitch; the field is situated in a basin of Tertiary age, surrounded by volcanic rocks, which vary from granite on the east to trachyte on the north, and columnar basalt on the west. Several basaltic hills and dykes protrude in different portions of the basin, and the presence of hot and mineral springs further testifies to the volcanic influences which have been at work and in which, doubtless, originated the boracic mineral. The latter occurs in a stratum at the bottom of an enormous bed of gypsum; its greater sp.gr. probably impelling it downwards, while the whole mass was yet in a soft state. Several feet of clay cover the gypsum bed, which is here 60 or 70 feet thick, though in places it attains to double that thickness. The borate strata vary in depth, and have been proved for a vertical distance of 45 feet. The mineral exists in closely packed nodules of very irregular size and shape, and of all weights up to a ton. It is easily separated from the dark-coloured gypsum in which it is embedded, and a number of people are employed at the pit mouth in picking and selecting the material. It is sold on a basis of 40 p.c. boric acid, which would be equal to 78·5 p.c. of the pure calcium borate with five molecules of water $Ca_2B_6O_{11},5Aq.$, the remainder consisting of calcium sulphate and other impurities.

Borate spar or *colemanite* has been extensively mined since 1883 at Calico, in San Bernardino county, California, 462 miles south-east of San Francisco. The geological formation of the surrounding hills consists of black lava, sandstones of different colours, gypsum, steatite, and calcium carbonate; it is found in veins and seams from 2 feet to 8 feet in thickness, in some cases dipping at an angle of 36°, and at others running into the hillsides almost horizontally. Its colour and streak is white-milky to transparent; hardness 3·5–4; sp.gr. 2·4; before the blowpipe it exfoliates, decrepitates violently, and melts imperfectly after considerable heating; it imparts a reddish-yellow colour to the flame, which changes to green. The fragments are obscurely rhombic and pulverise easily; it is wholly soluble in hot hydrochloric acid: from the solution boric acid crystallises on cooling. Lustre of the mineral is vitreous to adamantine. The veins and seams are interspersed with masses of calcium carbonate and magnesium silicate, from which, like the boracite, it has to be picked and selected.

Its formula is $Ca_2B_6O_{11},5Aq.$; it is sold on the basis of 40 p.c. boric acid. Average samples from the bulk vary in composition from 33·8 p.c. boric acid up to 41·2 p.c.; the following analyses may serve as examples of the general composition:—

BORATE SPAR.

Component parts	1	2	3	4	5
*Calcium borate $Ca_2B_6O_{11}5Aq.$ . .	66·2	70·4	75·0	78·00	80·80
Calcium carbonate $CaCO_3$ . .	16·3	15·1	11·6	8·75	7·17
Insoluble matter SiO_2 . . .	10·5	10·2	8·9	7·10	7·60
Remaining impurities MgO, &c. .	7·0	4·3	4·5	6·15	4·43
	10[illegible]	100·0	100·0	100·00	100·00
* = to boric acid	33·8 p.c.	35·9 p.c.	38·2 p.c.	39·8 p.c.	41·2 p.c.

Borate spar is also found in the neighbourhood of Furnace Creek, Inyo county, California; its outward appearance is frequently so exactly like calc spar as often to be mistaken for that mineral. Priceite has hitherto not been so extensively mined as boracite and colemanite; a mine of this mineral, however, exists at Lone Ranch, Cheteo, Curry, county Oregon, from which source, since the first cargo was extracted by E. L. Fleming in 1888, several hundred tons have been taken. It is found embedded in boulders of different size, the nodules varying in weight up to one ton. It is of a soft chalky nature, purely white, can be easily rubbed to powder, but is of a cohesive character; it is very soluble in sulphurous acid, hydrochloric acid, or acetic acid, yielding boric acid. The following analysis from bulk shows its composition:—

Boric acid B_2O_3	44·24
Lime CaO	30·91
Water H_2O	23·00
Magnesia MgO	0·65
Silica SiO_2	1·20
	100·00

Bechilite is a calcium borate found in the lagoons in Tuscany.

Its composition is represented by the formula $CaB_4O_7,5H_2O$.

Boronatrocalcite, Ulexite, tiza, cottonballs, hayesine $Ca_2B_6O_{11}Na_2B_4O_7,16H_2O$, is a soft, fibrous, silky mineral of a brilliant white when pure, generally found in nodules of a yellowish-white colour, varying in size from that of a Brazil nut to a potato. This curious mineral was first found in the nitre beds of Peru in small quantities, and was examined by Ulex in 1836. It was discovered in Tarapaca, 30 miles from Iquique, under the crust that covers the nitrate of soda beds. It has since been discovered in Chile, Bolivia, California, Nevada, Nova Scotia, and Persia.

Its composition is constant, containing, when pure:

Boric acid B_2O_3	43·1
Lime CaO	13·8
Soda Na_2O	7·7
Water H_2O	35·4
	100·0

The nodules are frequently found incrusted with a coating of sodium sulphate and salt, from which cause the percentage of boric acid in large parcels varies considerably, the average being from 18 to 25 p.c.

Chile has hitherto been the principal source of supply of this borax material. Ulexite, when in a state of fine division, is difficultly soluble in boiling water.

Calcium borosilicate. Datolite (*Howlite*). A siliceous borate of lime, colour white, streak white, opaque, of a chalky nature, found at Calico, San Bernardino county, California, and at Brookville, Nova Scotia. Composition:

Boric acid B_2O_3	44·22
Lime CaO	28·69
Silica SiO_2	15·25
Water H_2O	11·84
	100·00

Copper borate is readily obtained by treating a soluble borate in solution with copper chloride or sulphate. It is blue, and used in certain oil paints and also in the colouring of porcelain.

Iron borate. A hydrated borate of iron, *lagonite* $Fe_2O_3,3B_2O_3,3H_2O$, is found in the Tuscan lagoons.

Lead borates. By mixing concentrated solutions of lead nitrate and borax, the metaborate $Pb(BO_2)_2,H_2O$ is precipitated, and by the use of solutions of smaller concentrations Rose obtained many basic salts. They all melt on strong heating to colourless or light-yellow, highly refractive glasses, the hardness increasing with the boron content. Glasses may be obtained by fusing together lead oxide and boric acid in any proportions greater than 0·0725 equivalent of PbO to 1 equivalent B_2O_3, but below this limit an emulsion is formed on cooling.

Magnesium borates. *Stassfurtite* (*Szaibelyte*). This mineral occurs crystalline and massive, colour white, streak white, fracture conchoidal uneven, subtransparent, translucent, lustre vitreous inclining to adamantine, hardness 7, sp.gr. 2·83, pyro-electric, soluble in acids. It is found at Stassfurt, Prussia, embedded in the kainite beds, the composition being:

Boric acid B_2O_3	62·33
Magnesia MgO	27·03
Chlorine Cl	7·91
Magnesium Mg	2·73
	100·00

It is also found in nodules in grey limestone at Werksthal, Hungary, and at Danbury, Connecticut, United States.

Sussexite is a hydrated borate of manganese and magnesia found in Sussex county, New Jersey, United States. *Tourmaline*, found in different parts of the world in different colours, also contains a small percentage of boric acid.

Potassium borates. Atterberg distinguishes five different potassium borates: a monoborate $K_2O,B_2O_3,3H_2O$; three diborates $K_2O,2B_2O_3$ crystallising with 4, 5½, and 6 molecules of water respectively; and Laurent's pentaborate $K_2O,5B_2O_3,8H_2O$ (Zeitsch. anorg. Chem. 1906, 367).

Sodium borates. The only commercially important compounds are sodium diborate (*v. Borax*) and the perborate (*v. Perborates*). The metaborate $NaBO_2,4H_2O$ is readily obtained by fusing together the necessary proportions of boric acid and sodium carbonate, and crystallising.

Acid borates $Na_2O\cdot3B_2O_3$ and $Na_2O,4B_2O_3$ melting at 694° and 783° respectively may be obtained by fusing mixtures of borax and boron trioxide.

Sodium diborate, or Borax. Borax occurs in the crude state in what are termed borax marshes, which are generally the bottoms of dried-up lakes, or, where tincal is found, lakes that are nearly dried. The crude borax in the former instances is found lying on the surface of the plain, of a peculiar greyish-yellow colour, having a depth of from 1 inch to 18 inches. It is generally associated with other substances, both soluble and insoluble, as the table of analyses below shows.

At Jagadhri in Northern India, 37 miles S.E. of Umballa, there is a borax refinery, the product of which is shipped to Calcutta. The quantity of tincal and borax obtained from the districts of the Himalayan Mountains amounts to about 2000 tons per annum. The tincal deposits are of very ancient origin. In North America there are no less than ten deposits, five of them being in the State of California—at Saline Valley, Furnace Creek, and Armagora (in Inyo county), Slate Range (in San Bernardino county), and Lower Lake (in Lake county); the remaining five are in the State of Nevada—at Rhodes, Teels Marsh, Columbus, and Fish Lake (in Esmeralda county), and Salt Wells (Carson Lake, Churchill county).

COMPOSITION OF CRUDE BORAX FROM THE MARSHES.

—	1	2	3	4	5	6	7	8
Sodium biborate	30·30	38·3	2·10	53·08	1·9	33·30	6·52	45·20
Water	37·68	40·8	14·08	39·24	25·7	25·88	16·46	43·80
Sand and insoluble matter .	18·00	10·9	12·80	1·20	33·0	2·40	8·80	7·15
Sodium carbonate . . .	6·10	5·3	16·10	5·50	34·3	13·70	18·30	2·75
Sodium sulphate . . .	0·26	0·1	19·10	0·35	0·5	8·25	20·22	—
Sodium chloride . . .	0·50	0·4	34·60	0·50	0·7	15·40	28·20	0·40
Calcium carbonate . . .	3·28	2·4	0·70	—	2·0	0·60	0·80	0·30
Magnesium carbonate . .	2·26	0·4	0·30	—	0·6	0·30	0·50	0·30
Oxide of iron and alumina .	1·62	1·4	0·22	0·13	1·3	0·17	0·20	0·10
	100·00	100·0	100·00	100·00	100·0	100·00	100·00	100·00

Borax was first accidentally discovered in California, in 1856, by Dr. John A. Veatch, since which time the different deposits mentioned have been developed, and the available supply is practically unlimited, and is solely regulated by the demand. The exports of borax from America have increased very greatly of late years, and, to a large extent, have taken the place of the Italian product.

Commercially, borax is valued by evaporating to dryness a known weight of the sample with hydrochloric acid, and estimating the chloride volumetrically in the residue with silver nitrate. Any chloride present in the sample as impurity is estimated separately and allowed for, the percentage of borax being calculated from the equation

$$Na_2B_4O_7+2HCl+5H_2O=2NaCl+4H_3BO_3.$$

Properties.—Borax forms two varieties of crystals, (1) the *decahydrate*, which is produced by allowing solutions of borax to crystallise by cooling down to the ordinary temperature; (2) *octahedral borax*, which is a pentahydrate which separates out when the solution is allowed to crystallise above 50°.

1. *Ordinary or prismatic borax* $Na_2B_4O_7,10H_2O$ forms large transparent monoclinic prisms with truncated lateral edges. They effloresce when exposed to the air, have a rather sweet cooling alkaline taste, and a sp.gr. of 1·75. When heated they melt in their water of crystallisation, swell up, and leave a porous spongy mass, called burnt or calcined borax (*borax usta*), and fuse at a red heat to a colourless anhydrous glass (vitrified borax) with a sp.gr. of 2·36, which gradually absorbs water from the air, reforming prismatic borax. At 62° the decahydrate undergoes transition into the pentahydrate $Na_2B_4O_7,5H_2O$ At 130° the salt contains 3 mols. H_2O, at 150°, 2 mols. H_2O; at 180°, 1 mol. H_2O. At 318° it becomes anhydrous.

When borax is distilled with methyl alcohol, about 50 p.c. of the boric acid comes over fairly readily, and on longer treatment nearly 60 p.c. From the liquor remaining in the flask, crystals of $NaBO_2,5CH_3OH$ separate (Polenske, Analyst, 1902, 34).

Borax dissolves in water, but is insoluble in alcohol. The aqueous solution has an alkaline reaction, and changes the colour of an alcoholic solution of turmeric to brown; a small quantity of a mineral acid restores the original yellow colour, but a larger quantity liberates boric acid in sufficient quantity to produce the characteristic brown colouration. The following determinations of its solubility are those of Horn and van Wagener (Amer. Chem. J. 1903, 346):—

t°	100 grams H_2O dissolve of anhydrous borax $Na_2B_4O_7$	t°	100 grams H_2O dissolve of anhydrous borax $Na_2B_4O_7$
5°	1·3 gram	60°	19·9 grams
21·5°	2·8	70°	24·4
30°	3·9	80°	31·4
45°	8·1	90°	40·8
50°	10·5	100°	52·3
55°	14·2		

For conditions determining the crystallisation of borax, *see* Levi and Castellani (Gazz. chim. ital. 1901, 40, i. 138).

At the temperature of 27°, borax solutions hold 1 lb. of borax to the imperial gallon, and have a sp.gr. of 1·500, or 10° Tw. The general crystallising strength is 1·160 sp.gr., or 32° Tw., when the solution holds [illegible] lbs. of borax to the gallon, crystallisation commencing at 65·5°.

Borax is easily decomposed by acids. *Hydrochloric acid* leaves, on evaporation, sodium chloride and free boric acid. *Carbonic acid* is absorbed by a solution of borax from the air, and no borax is precipitated on the addition of alcohol. Saturated with *sulphuretted hydrogen* and mixed with alcohol, the liquid separates on the addition of ether into two layers, the lower containing sodium sulphide, the upper free boric acid.

It forms double salts with arsenious acid of the empirical formula.

$$3Na_2O{\cdot}6B_2O_3{\cdot}5As_2O_3+10Aq$$

(Schweizer, J. 1850, 257). With *sodium fluoride* it forms sodium fluorborate. When 1 pt. tartaric acid is mixed with 2 pts. of a hot solution of borax, boric acid separates out on cooling. If the tartaric acid be increased, the separation of boric acid likewise increases up to a certain point, after which it diminishes, and ultimately is no longer separated. *Acid tartrate of potassium* forms a double salt with borax. *Silicic acid* is insoluble, or nearly so, in solutions of borax.

Benzoic, tartaric, and gallic acids dissolve more readily in borax than in water. Many fatty acids and resins dissolve as readily in borax as in alkaline leys, the borax behaving like a mixture of boric acid and free soda.

Borax fuses at 730° and readily dissolves and unites with metallic oxides, forming a fusible glass of a double salt, which property renders it of great use in soldering and in metallurgical operations and in blowpipe analysis, the glasses thus formed often exhibiting characteristic colours. It is used also in the preparation of easily fusible glass fluxes for enamels and glazes.

2. *Octahedral borax* $Na_2B_4O_7,5H_2O$ is obtained by allowing a saturated solution of borax to cool down to about 60° in a warm place and removing the crystals.

The crystals are regular, transparent octahedra, harder than the ordinary borax. They have a conchoidal fracture and a sp.gr. of 1·8. They do not change in dry air, but absorb moisture very readily and become prismatic. They fuse more readily than the prismatic crystals, and with less intumescence, and without splitting. Octahedral borax is therefore better adapted for soldering and as a flux than common borax, and the smaller quantity of water (a difference of 17 p.c.) diminishes the cost of transport. The prismatic variety is, however, generally preferred, probably because it is cheaper weight for weight.

The commonest impurities in borax are sodium carbonate and small quantities of chlorides and sulphates of sodium, calcium, and magnesium. It is occasionally adulterated with earthy matters, alum, and sodium chloride. It should dissolve in two parts of boiling water and should not effervesce with acids. The aqueous solution should not be rendered turbid when treated with an alkali, or with barium chloride or silver nitrate in presence of nitric acid.

The manufacture of borax from boric acid.

This industry is chiefly associated with the production from the Tuscan lagoons. The crude acid, packed in large casks weighing about 13 cwts., on arrival at the borax works is first of all manipulated in the casks themselves. For this purpose, the cask is placed on what is termed a stillage, the head taken off, the acid loosened with a spade and treated with small quantities of water for the purpose of washing out the sulphates of ammonia and magnesia, which, on account of their greater solubility, easily separate from the less soluble boric acid, the washings being used for the recovery of the ammonia and magnesia they contain, whilst the acid, which formerly contained 83·46 p.c. $B_2O_33Aq.$ or equivalent to 128·5 p.c. borax, is brought up to a strength of 96 67 p.c $B_2O_33Aq.$ or equivalent to 148·87 p.c. borax. The acid, after draining for twenty-four hours, is then placed in wicker baskets and transferred to the saturators. These are made of wrought-iron ⅜ plates, having a diameter of 10 feet, egg-ended, height 9 feet 6 inches, provided with hopper and swivel discharge, still head, inspection glasses, run-off stop-cocks, and connected by steam pipes with a perforated iron coil in the bottom of the pan for the purpose of boiling the borax liquor with injected steam. There is also a manhole with movable cover. When the saturator is ready for charging, liquor is pumped in to the height of 4 feet, or 2300 gallons, which is then boiled with steam and soda ash. Anhydrous sodium carbonate is then added, about 23 cwts. being generally required to 60 cwts. of acid. When the soda ash is all dissolved, the manhole lid is placed on, and the boric acid is put in by degrees through a hopper, half a hundredweight at a time. At each addition of acid a brisk ebullition of carbonic acid takes place, which passes along the still head, and after being deprived of its ammonia may be utilised for making bicarbonate of soda.

After the saturator has received its charge of soda ash and acid, the liquor is thoroughly boiled for five hours and allowed to settle, in order that the solid impurities may subside. This generally occupies from eight to ten hours, after which the liquor is run into large wrought-iron vats 12 feet long, 6 feet wide, 4 feet deep, into which the wires made of iron, technically called 'straps,' are suspended over bars of wood laid across the top of the vat. The liquor on cooling crystallises on the wires, sides, and bottom of the vat, and when the temperature has fallen to 26° (80°F.), the liquor is siphoned off from the vats, and men get in, and, by the aid of iron bars terminating in a chiselled end, first remove the crystallised borax from the straps, then cut up the borax crystallising on the bottom of the vat, and lastly knock down the sides. This borax is not of sufficient purity for the market, and is, therefore, subjected to a second refining, and, if necessary, bleaching. For this purpose a series of pans, called refining pans, are employed; they are also of wrought iron, circular, 9 feet diameter, egg-ended, 8 feet deep open at the top and provided with cradles of wrought iron perforated with holes, suspended by iron chains from a patent block overhead in such a manner as to be raised or lowered in the pans as required. The pans are boiled with steam issuing from a perforated pipe in the bottom. They are first half filled with water, or some of the clearest liquor from a previous operation, and when the liquor is boiling crude borax is thrown into the cradle and allowed to dissolve. The right amount of borax is tested by means of the Twaddell hydrometer, which should read 30° when the liquor is of the required strength. About 5 cwts. of sodium carbonate is added, and a little chloride of lime, and the whole thoroughly boiled. The saturated liquor is then allowed to settle in the pans for ten hours, covers being placed on them to prevent the liquor chilling; the pans are run off into vats of similar size and shape to those employed in the first process, and the borax allowed to crystallise, which takes six days. Upon the expiration of that time, the liquor is siphoned off to a well, made by sinking a wrought-iron tank in the ground below the level of the vats, and, if impure, is pumped up to the refining pans to be used over again, and if sufficiently pure is pumped to boiling-down pans, to be concentrated to such a degree as to yield a further crop of borax.

The liquors from the first vats are also pumped to the boiling-down pans, where they likewise undergo a process of concentration. These boiling-down pans are made of wrought iron, and are capable of holding about 4000 gallons. They are provided with dry-steam coils, and are superior to other means of concentration from the fact that they are completely under control, and the evaporation of the liquor can be regulated as fast or as slow as may be necessary. The liquors in these pans are concentrated until they reach a sp.gr. of 1·300, or 60° Tw., when they are run off into vats to yield first a crop of borax, and then upon reaching a temperature of 80°F. they are siphoned off into other vats, where they yield a crop of Glauber salts, or sodium sulphate, after which the liquors, being rich in sodium carbonate, are used again in the saturators for making up a fresh batch of borax with acid and soda ash. The mother liquors, strong in common salt and weak in sodium carbonate, are further concentrated in jacketed pans, where, on continued boiling, the salt falls to the bottom, is collected by means of rakes, and fished out with perforated scoops provided with long wooden handles, and the salt is ladled into iron baskets set over the pans and allowed to drain. By this means all the salts contained in the soda ash and boric acid are saved, and nothing is run to waste.

The washings from the boric acid in the first process, containing the ammonium sulphate and magnesium sulphate, are collected together, and placed in a wrought-iron still provided with a dry-steam coil. The requisite amount of sodium carbonate is then added, and the ammonium carbonate is distilled off, yielding a highly concentrated and very pure carbonate of ammonia liquor, which is either sold in that state or utilised for making the purest volcanic ammonia salts.

The borax from the refined vats, consisting of the straps and sides, is carried to the packing room, there to be picked, selected, and packed in casks, whilst the borax bottoms, not being in the form of merchantable borax, are refined again.

Manufacture of borax from borate of lime.

The mineral is first crushed in a stone breaker, the size of jaw being 8 inches and known as No. 4, easily capable of crushing 12 tons in twenty-four hours. As the mineral passes through it is taken up by an elevator and run through millstones, 30 inches in diameter, and placed by the side of the crusher. There are two pairs, one grinding fresh ore and the other grinding the tailings. The millstones deliver the powdered ore into another elevator, which passes it through a bolting or sifting machine, 10 feet long and 30 inches in diameter, having octagonal sides, the bolting cloth being of silk known as No. 8. As considerable fine and impalpable dust arises from the sifting, it is kept down by means of an exhaust fan blowing the dust into a dust room. The fine mineral is conveyed by means of an Archimedean screw and elevator into bins, each holding a certain quantity and placed over the saturators. These are wrought-iron tanks capable of holding a charge of 2500 gallons, and provided with suitable agitators and either dry or wet steam coils, the bottom of the saturators being connected by 3-inch wrought-iron valves and pipes to a powerful pump for the purpose of removing the contents of the saturator when desired. The saturators are grouped together in sets of four for facilitating the lixiviation of the contents by means of repeated washings, after the first decomposition of the mineral. The saturators, as in the case of the manufacture of borax from boric acid, are first charged with liquor and brought to the boil; a charge of soda ash, usually about 30 cwts., being put in, which is sufficient to decompose three tons of the borate of lime which is gradually added after the soda ash is all dissolved. The soda ash gradually but completely decomposes the sesquiborate forming calcium carbonate, borate of soda, and biborate of soda:

$$Ca_2B_6O_{11}+2Na_2CO_3 = 2CaCO_3+Na_2B_4O_7+2NaBO_2.$$

After boiling five hours the steam and agitators are stopped, and the muddy liquor allowed to settle for ten hours, after which time the clear supernatant liquor is run off to vats to crystallise, and the residue is again washed with weaker liquor from the saturator previously washed, the operation being repeated of boiling and washing with the gradually weaker liquors from the other saturators in rotation. By the time the mud has received eight washings, the last being with water, the whole of the borax will have been removed, and the chalk which is left is then pumped through an iron filter press, which completely presses out the remaining weak liquor and leaves the chalk in a solid cake, which is generally thrown to one side, being too impure for any purpose. The first liquor run to the vats contains the biborate and borate of soda, together with carbonate and sulphate of soda in solution. The biborate of soda or borax crystallises out after cooling in the vats for about six days, leaving the borate of soda in solution. The liquor is then siphoned off into the well and pumped to the boiling-down pans, where it undergoes the process of concentration until it reaches a sp.gr. of 1·350 to 1·400 (70° to 80° Tw.), when it is run off into vats and allowed to throw a further crop of borax. The mother liquor is now of a syrupy consistence, and is pumped into a decomposing tank, where carbon dioxide is blown through it. The following decomposition takes place:— a finely divided state, whilst the sodium carbonate remains in solution, and can be used over again in the saturators for the first operation. The refining of the borax from the first process is the same as that employed in the boric acid process, and therefore need not be further described. The only precaution necessary is the addition of a little bicarbonate of soda in the pans to decompose any borate of soda that might be associated with the borax. Three tons of borate of lime produce 2 tons of borax and 1 ton of borax in the state of metaborate of soda. Metaborate of soda may be formed by mixing the concentrated solutions of borax and caustic soda together in their equivalent quantities, and evaporating to 70° Tw.:

$$Na_2B_4O_7+2NaHO=4NaBO_2+H_2O$$

from which the metaborate of soda crystallises in needle-shaped crystals having the formula $NaBO_2,4H_2O$.

100 parts of metaborate of soda, when decomposed by carbonic acid, produce 65·6 parts of borax and 34·4 parts of sodium carbonate; about 30 cwts. of borate of soda thus produce 20 cwts. of borax.

The following process is used by Masson, Gembloux, and Tillière, Brussels. An ammonium salt is treated with lime in a distilling column and the ammonia set free is passed into water contained in a digester, and the digester is then charged with carbonic or sulphurous acid. The digester is gently heated and pandermite is introduced. It is then closed and more strongly heated for several hours, whilst the contents are mechanically agitated and are transferred, when the action is complete, to filter presses, whence the liquor passes to a reaction chamber where it is agitated with sodium chloride and, after addition of a little ammonia, is discharged into crystallisers. After removal of the borax which crystallises out, the mother liquor is used instead of water in the succeeding operation. After several operations, the mother liquor requires a special treatment.

In this process, an ammonium biborate is first obtained by the ammonium carbonate treatment of calcium borate, and from this ammonium salt borax is obtained by double decomposition with sodium chloride. Boronatrocalcite may be used instead of pandermite if the process is slightly modified.

Manufacture of borax from ulexite.

Borax is manufactured from this mineral at the various deposits, and also in England, France, and Germany, to which places it is exported from Chile and California, selected and packed in sacks.

The first operation consists in reducing the material to a state of fine division, and for this purpose a mill is used so constructed as to tear the borate to pieces instead of grinding it, which, owing to its fibrous silky nature, is found preferable.

The borate is then mixed with its proper proportion of soda ash and bicarbonate of soda, or soda ash and boric acid, having regard to the fact that, if associated with much gypsum, a proportionate additional allowance of soda ash must be made, as the gypsum decomposes the and chalk. The composition of ulexite being $Ca_2B_6O_{11}\cdot Na_2B_4O_7$, it requires one equivalent of bicarbonate of soda and one equivalent of carbonate of soda to decompose it:

$$2(Ca_2B_6O_{11}Na_2B_4O_7)+2NaHCO_3+2Na_2CO_3$$
$$=5Na_2B_4O_7+4CaCO_3+H_2O.$$

These ingredients are all mixed together in the dry state. The process adopted is similar to the processes already described—namely, that of first boiling the liquor in the saturator, then gradually adding the crude material, boiling, settling, lixiviating.

100 parts of the ulexite, testing 43 p.c. boric acid, require 10 parts of bicarbonate of soda and 12 parts of carbonate of soda, for its conversion into 117 parts of borax.

Manufacture of borax from crude borax.

This branch of the industry is generally carried on at the borax marsh. It may be desirable to give a description of the Saline Valley, Inyo county, California, where the most extensive deposit of natural borax exists in North America, before entering into the details of refining.

The valley, situated on the eastern slope of the Sierra Nevada Mountains, 11 miles from the Carson and Colorado railroad, is 18 miles long and 12 miles wide, surrounded with mountainous hills which afford no outlet, and therefore the valley may be said to be the bottom of a dried-up lake. At the point of deepest depression an area of over 1000 acres is covered with crude borax from 6 to 18 inches in depth. The colour of the crude material as it lies upon the level plain is a peculiar grey yellow. The borax in Saline Valley is mixed with sand, which is volcanic ash and decomposed lime rock, sodium sulphate, sodium carbonate, and sodium chloride. The surrounding hills consist of granite, marble, dolomite, black lava, and felspar. The composition of the crude material varies in strength from 10 p.c. of borax up to 90 p.c., whilst in some places on the marsh—under a crust composed of sodium sulphate, sodium carbonate, and common salt—beds of tincal, or large crystals of borax, some two feet in thickness, are found; whilst below the tincal there is a strong saturated yellowish liquor containing 1 lb. of borax to the gallon. All the manipulation that is required is to shovel off the surface of the marsh to a depth of 18 inches and cart the material to long hemispherical wrought iron pans set on arches of stone, fired beneath with wood fuel obtained in the neighbourhood. The pans are charged with water, and the crude material thrown in and vigorously stirred with long poles, until, with the aid of heat, all the soluble salts are dissolved. The fires are then withdrawn, and the contents of the pans allowed to settle for ten hours, when the liquor is drawn off into vats, where the borax crystallises out. The mother liquor after six days is drawn off, and the borax is taken out and packed into sacks for shipment.

Borax and boric acid are applied in the manufacturing industries as follows:—

Brick and tile makers. Glazed surfaces.

Candle makers. Preparation of wicks.

Cement. Making the finest kinds, which take a polish.

China and earthenware. In preparing a frit used for glazing what is technically termed 'biscuit ware' in pottery of all descriptions.

Colour makers. In preparing Guignet's green and borate of manganese (a drier).

Coppersmiths. In brazing.

Druggists. Pharmaceutical preparations.

Enamelled iron. An enamelled coating to cast and wrought iron.

Glass. Making pastes and as an ingredient.

Hat makers. Dissolving shellac for a stiffener.

Ironsmiths. In welding.

Jewellers. In soldering. (Ancient name for borax, 'chrysocolla,' gold-glue.)

Laundresses. As a starch-glaze for linen.

Paper makers. Superfine note and highly glazed paper and cards.

Pork packers. Curing and preserving hams and bacon.

Safe makers. Lining safes to resist fire.

Soap makers. As an emollient.

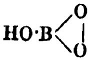
Tanners. Dressing leather.

Textile manufacturers. Solvent-bleach; mordant; fireproofer.

Timber merchants. In preparation of hard from soft wood.

Zinc borate is formed by adding borax in slight excess to a solution of a zinc salt. For conditions of formation, *see* Borchers (Zeitsch. anorg. Chem. 1910, 68, 269).

Perborates are salts of the acid HBO_3 or



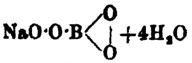
$$HO\cdot B\begin{matrix}\diagup O\\ \mid\\ \diagdown O\end{matrix}$$

which has not been prepared in the free state on account of its instability. The alkali and alkaline earth salts are soluble in water and have an alkaline reaction. They behave in solution like mixtures of borates with hydrogen peroxide; the active oxygen being liberated by heat, by acidifying the solution, or by large dilution. Oxydases, reductases, and manganese dioxide cause them to give up the whole of their reactive oxygen. They convert chromic acid and molybdates into perchromic acid and yellow permolybdates. They readily oxidise protoxides and their salts into higher oxides, but do not always form perborates with them. Ferrous, mercurous, manganous, and lead salts yield higher oxides; the salts of other metals yield perborates of an indefinite or basic composition. Perborates of the alkali metals may be obtained by careful precipitation of solutions of alkali borates with alcohol in the presence of hydrogen peroxide.

Ammonium perborate NH_4BO_3,H_2O is the best characterised of the several perborates resulting from the action of ammonia and hydrogen peroxide on ammonium borate. It contains 16·84 p.c. of active oxygen.

Potassium biperborate $KB_2O_5,2H_2O$ is obtained by the action of hydrogen peroxide on potassium borate.

Sodium perborate $NaBO_3,4H_2O$. When 248 grams of boric acid are mixed with 78 grams of sodium peroxide and added gradually to 2 litres of cold water, the mixture dissolves at first, but later a crystalline substance separates out which may be filtered off and dried. This substance, which has a composition $Na_2B_4O_8,10H_2O$, is called '*perborax*,' and is soluble in water to the extent of 42 grams per litre at 11°. When one-half of its sodium is displaced by a mineral acid, a crystalline precipitate of *sodium*



perborate, $\mathrm{NaO{\cdot}O{\cdot}B}\left\langle\begin{matrix}\mathrm{O}\\|\\\mathrm{O}\end{matrix}\right. + 4\mathrm{H_2O}$ separates out. This is a very stable substance, and can be preserved indefinitely at ordinary temperatures. It dissolves readily with slight decomposition in water at 50°–60°, and a vigorous ebullition of oxygen takes place at 100°. The cold aqueous solution possesses all the properties of hydrogen peroxide. When powdered sodium perborate is added gradually to 50 p.c. sulphuric acid, and the solution filtered through guncotton a very strong (150–200 vols.) solution of hydrogen peroxide is obtained.

For the constitution of the perborates, *see* Bosshard and Zwicky, Zeitsch. angew. Chem. 1912, 25, 993.

ORGANIC DERIVATIVES OF BORIC ACID.

Aniline borate, and compounds of *piperidine, conine, tetrahydroquinoline*, and *tetramethylammonium hydroxide*, have been prepared by L. & T. Spiegel (J. Soc. Chem. Ind. 1905, 103). The *menthyl* and *bornyl* esters are readily prepared by heating menthol and borneol with boric acid, xylene being used as a medium in the latter case (Verein Chininfabriken, Zimmer & Co., Eng. Pat. 11574, 1906).

Ethyl borosalicylate, or '*boryl*,' is prepared by boiling together 62 grams of boric acid and 138 grams of salicylic acid with 200 c.c. of water. The resulting borosalicylic acid is esterified by adding 60 grams of 95 p.c. alcohol and heating with 40 grams of sulphuric acid. It forms needle-shaped crystals which are more convenient than oil of winter-green for many medicinal purposes (Cohn, Chem Zentr. 1911, 1; 1806).

Zinc boropicrate, or '*chrysyl*,' is the product obtained by boiling together boric and picric acids, and saturating the mixture with zinc oxide. It is a yellow powder used as a medicinal antiseptic (Monteil, J. Soc. Chem. Ind. 1908, 354).

Phenyl borate $\mathrm{B(OPh)_3}$, *diphenylboric acid* $\mathrm{B(OH)(OPh)_2}$, *m-tolyl borate* $\mathrm{B(OC_6H_4Me)_3}$, and *β-naphthyl borate* $\mathrm{B(C_{10}H_7O)_3}$, together with several other aryl halogen boron compounds and *p-borobenzoic acid* $\mathrm{CO_2H{\cdot}C_6H_4{\cdot}B(OH)_2}$, have been prepared by Michaelis (Annalen, 315, 19–43).

Borcitrates are valuable as remedies in cases of kidney disease and urinary calculi. Their solvent power for urates and phosphates is greater than that of lithium benzoate. The diborocitrates are best adapted for the purpose. The following are known:—

Magnesium triborocitrate $\mathrm{(C_6H_5O_7)_2Mg_3(B_3H_3O_6)_2}$
" diborocitrate $\mathrm{(C_6H_5O_7)_2Mg_3(B_2H_2O_4)_2}$
" monoborocitrate $\mathrm{(C_6H_5O_7)_2Mg(BHO_2)}$

Lithium, potassium, sodium, and ammonium, mono-, di-, and tri-borocitrates of similar constitution have been prepared. Iron salts have also been obtained containing respectively 8 and 16 p.c. of iron by acting on sodium di- and mono-borocitrate with ferric hydrate (Scheile, Pharm. J. [3] 11, 389).

The magnesium compounds possess strong antiseptic properties.

DETECTION AND ESTIMATION OF BORON.

Boron almost always occurs in the form of boric acid. When the acid is in the free state it can readily be recognised by the green colour which it gives to the flame, and by its action upon turmeric.

Turmeric paper, when moistened with a solution of boric acid and dried, acquires a cherry-red colour, which is changed to olive-green on moistening with an alkali. Acid solutions of zirconic, tantalic, niobic, and molybdic acids also colour turmeric brown. Cassal and Gerrans (Chem. News, 1903, 27) find that the sensitiveness is greatly increased by the addition of oxalic acid, and base a colorimetric method of estimation of boric acid on this reaction.

The green colour imparted to flame is a very delicate test for boron (according to Merz, J. pr. Chem. 80, 487, 1 part in 1400 may be detected by means of it). It is, however, to be noted that salts of copper likewise colour flame green, as well as certain compounds of chlorine and barium and thallium. When the boric acid is combined with a base the compound in the state of powder is decomposed by means of sulphuric acid, and the boric acid extracted by alcohol. Compounds not decomposed by sulphuric acid are fused with potash and digested with alcohol and sulphuric acid.

The presence of boron in minerals may be detected by mixing the mineral in powder with a flux containing 1 part fluor-spar to 4½ parts hydrogen potassium sulphate, made into a paste with water, and heating the mixture in the inner blowpipe flame, when boron chloride is given off which tinges the flame green; or by mixing the suspected substance with fluor-spar moistening with concentrated sulphuric acid, and passing the escaping gas through a tube drawn to a fine point into the non-luminous bunsen flame, which it colours green.

The spectrum of boron shows three bright lines in the green and one in the blue. Hartley finds in the spectra of boric acid and borax the lines λ3450·3, λ2497, and λ2496·3, which he considers characteristic of boron (Roy. Soc. Proc. 35, 301). (For the measurement of the intensity of these bands, *v.* Lecoq de Boisbaudran, Compt. rend. 76, 883.)

The quantitative estimation of boron is difficult, as all borates are soluble to some extent in water and alcohol, and boric acid cannot be heated without loss in contact with water.

One method of direct determination is to precipitate the boron as potassium borofluoride, which is quite insoluble in alcohol (Berzelius, Lehrbuch, 3 ed. 10, 84; Stromeyer, Annalen, 100, 82; Thaddeeff, J. Soc. Chem. Ind. 1898, 953). This method has been adversely criticised by Gooch and others, and has been almost entirely superseded.

The most trustworthy method of estimating boron is due to Gooch. If the boron is not present as boric acid, it is brought into that state by heating for some hours in a sealed tube with nitric acid. The resulting solution is repeatedly distilled with methyl alcohol, the boric acid passing over in the vapour. The distillate is then treated with an exactly weighed excess of pure lime, transferred to a platinum crucible, evaporated to dryness on the water-bath and strongly heated. The increase in weight represents the boric anhydride.

Volumetrically, boric acid may be estimated accurately by titration with caustic soda, using phenolphthalein as indicator, if about one-third of the bulk of the solution of glycerol is added (Thomson, J. Soc. Chem. Ind. 1894, 432; *v.* also ANALYSIS).

A freshly prepared solution of manna may replace the glycerol (Iles, Analyst, 1918, 43, 3257). Tropaolin O (sodium-*p*-benzene-azoresorcinol sulphonate) may be used for the direct titration of boric acid without the addition of mannitol or glycerol. Soda is first neutralised by standard hydrochloric acid in the presence of methyl orange or *p*-nitrophenol, excess of sodium chloride not materially interfering with the accuracy of the method. The indicator is introduced as 0·04 p.c. solution (Prideaux, Zeitsch. anorg. Chem. 1913, 83, 362).

Boron may be estimated indirectly by digesting a weighed quantity of the finely divided compound in a platinum vessel with hydrofluoric acid, and then with concentrated sulphuric acid. On warming gently, the boron present is expelled as fluoride, and after driving off the excess of sulphuric acid, the quantity of bases in the residue is determined. Their weight, deducted from the weight of the original substance, gives the quantity of boric anhydride.

When combined with potash or soda, boric acid may be determined by evaporating the solution of the previously weighed salt with hydrochloric acid, and determining the chlorine in the dry residue (Schweizer, Pharm. Centr. 1850, 372; J. 1850, 590)

Crude boric acid (Italian) is usually valued by determining the water and the substances insoluble in alcohol, and taking the rest as being boric acid. According to Zschimmer (Chem. Zentr. 1901, [5] 44, and [7] 67), the results are inaccurate, on account of the water not being completely driven off under the conditions used (2 hours drying at 45° and 2 hours in desiccator).

Boron is best estimated in the presence of silicates; *e.g.* in tourmaline, by the method of G. W. Sargent, who has submitted all the processes published to examination and criticism (J. Amer. Chem. Soc. 1899, 858–888). The mineral is fused with alkali carbonates, and, after lixiviating and acidifying, the boric acid is volatilised from the solution as the methyl ester. A convenient form of apparatus for performing this operation is described. The boric ester is subsequently hydrolysed by a weighed quantity of pure lime, and estimated by Gooch's process.

A method for its estimation in insoluble silicates is also given by Wherry and Chapin (J. Amer. Chem. Soc. 1908, 1687–1701).

A solution of boric acid produces no change of colour in solutions of helianthin, tropæolin, and methyl orange, but a drop of hydrochloric acid immediately changes the yellow colour into red. Borax may thus be titrated by the stronger acids (A. Joly, Compt. rend. 100, 103).

(For the estimation of boric acid in mineral waters, *v.* Fresenius, Zeitsch. anal. Chem. 25, 202.)

To detect boric acid in milk, baryta is added to 100 c.c. of milk till alkaline. After incineration, the ash is dissolved in a little strong hydrochloric acid, evaporated to dryness, and a solution of turmeric with a drop of dilute hydrochloric acid added, and the solution evaporated on a water-bath. 0·001 c.c. boric acid gives a distinct colour to turmeric in this manner (J. Soc. Chem. Ind. 1887, 563).

Boric acid may be rapidly determined in butter by stirring a weighed quantity with a known volume of warm standard sulphuric acid till melted, allowing to settle, and titrating a portion of the aqueous part with caustic soda, using phenolphthalein. The pink colour appears when the sulphuric acid has been neutralised; glycerol is then added and caustic soda run in till the colour reappears. The second titration represents the boric acid (Richmond and Harrison, Analyst, 1902, 179).

BORONATROCALCITE. An early name (G. L. Ulex, 1849) for the mineral ulexite, a hydrated borate of sodium and calcium $NaCaB_5O_9,8H_2O$. Most of the natural borates exported from South America (Chile, Bolivia, and Argentina) are of this species; it is also abundant in the borate deposits of California and Nevada. L. J. S.

BOROVERTIN *v.* SYNTHETIC DRUGS.

BORSALYL. Trade name for sodium borosalicylate.

BORYL. Trade name for ethyl borosalicylate. Prepared by boiling together solutions of boric acid and salicylic acid and esterifying by the addition of alcohol and sulphuric acid. Needle-shaped crystals. Used in medicine as a substitute for ethyl salicylate (Monteil, J. Soc. Chem. Ind. 1908, 354).

BOSCH. An inferior butter prepared in Holland. The term is sometimes used as synonymous with margarine (*q.v.*).

BOSTONITE. A trade name formerly in use for the Canadian serpentine-asbestos (*v.* ASBESTOS). L. J. S.

BOSWELLIA SERRATA (Roxb.) or **GUGAL.** The gum of this plant (ord. *Burseraceæ*) is used as an incense. It is often confounded with bdellium and olibanum (Dymock Pharm. J. [3] 7, 190).

BOTANY BAY RESIN *v.* BALSAMS.

BOTRYOLITE *v.* CALCIUM.

BOTTLE-NOSE OIL. An oil obtained from the bottle-nosed whale, closely resembling sperm oil; its sp.gr. varies from 0·876 to 0·880 (Allen, J. Soc. Chem. Ind. 2, 53).

BOUILLON NOIR. *Ferric acetate* (*v.* ACETIC ACID).

BOU-NEFA. The root bark of *Thapsia garganica* (Linn.), an umbelliferous plant growing in the South of Europe and Algeria. It contains a resin used as a medicine in France.

BOURNEENE or **VALERENE.** A liquid hydrocarbon isomeric with oil of turpentine, secreted by the *Dryobalanops aromatica* (Gaertr.), and holding in solution borneol or Borneo camphor. According to Wallach (Annalen, 230, 225; Chem. Soc. Trans. [2] 50, 70), it is a mixture of the decomposition products of camphene.

BOURNONITE. Sulphantimonate of copper and lead $CuPbSbS_3$, crystallising in tabular orthorhombic crystals; these are frequently twinned and show re-entrant angles at the edges, hence the names 'cogwheel-ore' and 'wheel-ore.' It is found in Cornwall, Harz, &c.; and in Bolivia. It sometimes occurs in sufficient abundance to be used as an ore of copper and lead. L. J. S.

BOVEY COAL *v.* FUEL.

BRAGA. An alcoholic beverage used in Roumania, prepared by the fermentation of millet. The seed is boiled with about 12 times its weight of water for 14 hours, the resulting viscous mass cooled, stirred with water and allowed to ferment. The liquid is filtered and mixed with water, when it is ready for sale. It is somewhat sweet, and contains about 1·3 p c. of alcohol by weight.

BRAIN'S POWDER. An explosive consisting of 60 parts of a mixture of potassium chlorate, potassium nitrate, wood charcoal, and oak sawdust saturated with 40 parts of trinitroglycerine (Wagner's Jahr. 22, 470).

BRAN. The name given to the coarser fragments, consisting mainly of the outer layers, which are produced in the grinding or milling of cereal or other seeds. When the term is used without any descriptive adjective, the product from wheat is usually understood; but maize, barley, buckwheat, rye, oats, even peas and earth nuts, when milled, yield products which are described as 'bran.'

The following analyses, compiled chiefly from German and American sources, show the general average composition of various 'brans':

—	Water	Protein	Fat	Sol. carbohydrates	Fibre	Ash
Wheat bran, fine	13·2	15·5	4·8	54·0	8·0	4·5
„ „ coarse	13·2	14·3	4·2	52·2	10·2	5·9
„ „ spring wheat	11·5	16·1	4·5	54·5	8·0	5·4
„ „ winter wheat	12·3	16·0	4·0	53·7	8·1	5·9
Rye bran (German)	12·5	16·7	3·1	58·0	5·2	4·5
„ „ (American)	11·6	14·7	2·8	63·8	3·5	3·6
Barley bran	10·5	14·8	3·6	57·6	8·5	5·0
Oat bran	9·6	7·6	2·7	53·8	21·6	5·7
Maize bran	12·5	9·9	3·6	61·5	9·5	3·0
Rice bran	9·7	12·1	8·8	49·9	9·5	10·0
Buckwheat bran, fine	12·0	15·2	4·5	50·0	11·3	7·0
„ „ coarse	15·6	8·0	1·8	34·2	37·6	2·8
Pea bran	11·7	16·8	1·7	46·2	20·1	3·5
Earth nut bran	10·5	21·8	18·1	24·7	19·5	5·4

The digestion coefficients for the constituents of most varieties of bran are low, so that their food value is in general not so high as the analyses would indicate.

The character and composition of the bran from any particular grain is liable to considerable variation, according to the method of milling adopted. As a rule, the less perfectly the corn is ground, the richer is the bran in meal and therefore in feeding value.

It will be noticed that bran is much richer in protein, fat, ash, and fibre than the fine portions of the meal from the same grain.

In the case of wheat, the finer portions of the bran are known as 'middlings' and 'sharps' or 'shorts.' Usually the last term denotes the portions which most nearly resemble bran, while 'middlings' refers to an intermediate product more approximating to flour in composition, though much richer in protein, ash, and fibre.

The processes employed in the milling of wheat, however, are so complex that about 80 or 100 products are separated. For a study of the composition of the various products of a modern roller mill, *see* Clifford Richardson (Bull. No. 4, U.S. Dept. of Agric. Div. of Chemistry, reproduced in part 9, Bull. 13, [1898]). Usually, about 70 to 75 p.c. of the wheat is obtained as flour of various grades, about 20 p.c. as bran, 3 or 4 p.c. as 'shorts,' and the remainder as screenings and loss.

Weinwurm (Oesterr-Ungar. Zeits. Zucker-ind. u. Landw. 1890) found that from Hungarian wheat, 20 p.c. of bran of three degrees of fineness were obtained, possessing the following composition:—

—	Yield p.c.	Water	Composition of dry matter					
			Protein Insol. in dil. acetic acid	Protein Sol. in dil. acetic acid	Fat	Sol. carbohydrates	Fibre	Ash
Fine bran	16	11·35	13·50	3·06	4·54	63·64	8·71	6·55
Medium bran	2	11·55	13·38	2·72	3·96	63·97	9·08	6·89
Coarse bran	2	12·37	13·44	3·17	3·46	62·13	9·79	7·01

Snyder (Studies on Bread and Bread-making at the University of Minnesota, 1901) examined the products from the milling of wheat by the American methods, using a hard Scotch Fife wheat.

The shorts and bran obtained had the following composition:—

	Water	Protein (N×5·7)	Fat	Total carbohydrates	Ash	Acidity
Shorts	8·73	14·87	6·37	65·47	4·56	0·14
Bran	9·99	14·02	4·39	65·54	6·06	0·23

The acidity is expressed in terms of lactic acid.

The carbohydrates of bran have been investigated by Sherman (J. Amer. Chem. Soc. 1897, 19, 291). He found the following average percentages in wheat bran:—

Total soluble carbohydrates calculated as dextrin	7·2 p.c.
Starch	17·7
True pentosans	17·5
Lignin and allied substances	11·6
Cellulose	8·5
Total carbohydrates	62·5

Other investigators — Tollens, Chalmot, Günther and Stone—have found from 22 to 25 p.c. of pentosans in wheat bran, while maize bran contains about 40 p.c.

Girard (Compt. rend. 1897, 124, 926) gives the results of the examination of by-products from wheat—presumably shorts and bran—by a method different from the conventional one.

In estimating the amount of water-soluble matter in products from seeds, he points out the necessity of using ice-cold water, otherwise the enzymes present may act upon the constituents of the seed, and greatly increase the amount of matter soluble in water.

The following are the mean figures calculated from analyses of the by-products from four French wheats :—

Water	Soluble in water	Insoluble in water
14·72	10·63	74·65

The matter soluble in water consisted of—proteids 2·70, carbohydrates 6·16, inorganic matter 1·77. The matter insoluble in water consisted of—gluten 4·55, starch 28·08, nitrogenous woody matter 5·70, fats 3·17, cellulose 30·22, inorganic matter 1·94, loss and undetermined 0·99.

The mineral matter in bran is very high as compared with that in the rest of the seed, being usually between 5 and 6 p.c., whilst that in flour is usually less than 0·5 p.c.

The ash of bran is particularly rich in phosphoric acid, but poor in lime. The following analysis by Wolff gives its usual composition :—

K_2O	Na_2O	MgO	CaO	P_2O_5	SiO_2
24·0	0·6	16·8	4·7	51·8	1·1

There is a widespread belief that bran is particularly well fitted, because of its richness in mineral matter, to supply the needs of animals with reference to the development and nutrition of bone. But from a study of a bone disease among horses and mules in South Africa, it has been deduced that for normal bone nutrition it is necessary that animals be supplied, in their rations, with phosphoric oxide and lime in approximately equal proportions by weight (Ingle, Jour. Comp. Path. and Therapeutics, 1907, March, also Jour. Agric. Science, 1908, 3, 22). From this point of view, bran is particularly ill suited to aid bone development, since it contains an overwhelming preponderance of phosphoric acid over lime, being in the ratio of 100 to 9 in the above analysis, while in some samples it is as high as 100 : 5·5. That bran has an injurious action upon bone nutrition when used in large quantities, is shown by the occurrence of a peculiar bone disease in horses known as 'bran rachitis' or 'millers' horse rickets,' observed in animals fed largely on bran.

The phosphoric acid in bran, however, does not exist entirely as metallic phosphates. According to Patten and Hart (Bull. 250, New York Agric. Expt. Station, 1904) about 68 p.c. of the total phosphorus is extracted by 0·2 p.c. hydrochloric acid solution, and of this, nearly the whole exists as anhydro-oxymethylene diphosphoric acid $C_2H_8P_2O_9$

$$=(OH)_2OPO-CH_2-O-CH_2-OPO(OH)_2$$

a substance first isolated by Posternak (Revue General de Botanique, 1900, 12, 5 and 65; Compt. rend. 1903, 137, 439). In bran, this acid exists in combination with magnesium, calcium, and potassium.

According to more recent views (Anderson, J. Biol. Chem. 1915, 20, 463, 475, 483, and 493; Robinson and Mueller, Biochem. Bull. 1915, 4, 100; Clarke, Chem. Soc. Trans. 1915, 360) the phosphorus in bran is mainly in combination with inositol, the triphosphate $C_6H_{15}O_{15}P_3$ and the hexaphosphate $C_6H_{18}O_{24}O_6$ being the most important. Anderson (*l.c.*) finds that wheat bran contains about 0·1 p.c. of inorganic phosphorus, *i.e.* about 11 p.c. of the total soluble phosphorus.

The free acid, when heated with mineral acids, or with the enzyme-*phytase* (*q.v.*), is hydrolysed, yielding inositol and phosphoric acid $3C_2H_8P_2O_9+3H_2O=C_6H_{12}O_6+6H_3PO_4$.

Bran is largely used as a food for farm animals, but has a weakening effect upon digestion if used in large quantities. It is more suitable as a food for fattening than for working animals. Owing probably to its mechanical action on the bowels, it has a purgative effect. If used largely for milch cows, it tends to make the butter soft. Similarly, large quantities of bran given to fattening animals tend to lower the melting-point of the body-fat. This is an advantage in the production of mutton or beef, but a disadvantage with bacon.

Bran is also largely used in tanning leather. (For a description of the process and of the changes occurring in the fermentation of bran so employed, *see* Wood and Wilcox, J. Soc. Chem. Ind. 1893, 422, and 1897, 510.) H. I.

BRANDY. (*Eau-de-vie*, *Fr.*; *Branntwein*, Ger.) The term 'brandy' is an abbreviation of 'brandy-wine' the original English form of the word, which occurs also in all the Teutonic languages of Northern Europe, and signifies burnt or distilled wine. The latter term (wine) in its widest sense includes the product obtained by fermentation of all natural fruit juices or extracts from grain, and not fermented grape juice only. Old English Acts of Parliament refer to 'brandy' and 'aqua vitæ' made from malted corn, whilst the German word *branntwein* is applied to strong potable spirits generally without implying that such spirit is necessarily derived from wine. At the present time, however, the 'brandy' of commerce is almost universally understood to be a spirit derived exclusively from the grape.

Besides alcohol and water, the principal constituents of brandy are acetic, butyric, œnanthic, and valerianic esters, acetic acid, a small quantity of a volatile oil, and a little fixed acid, tannin, and colouring matter. When new, brandy is colourless, but gradually acquires a yellowish-brown colour by storage in oak casks. The required colour for particular brands is, however, usually obtained by the addition of a solution of caramel or burnt sugar. Genuine brandy of good quality has a sweet mellow ethereal flavour, without any suspicion of the 'fiery' or 'earthy' taste common to inferior or fictitious brandies.

The *bouquet* of brandy depends upon (*a*) the nature and quality of the wine from which it has been produced; (*b*) the conditions under which the wine has been fermented; (*c*) the method of distillation employed; and (*d*) the age of the brandy. The characteristic flavour of brandy is said to be due chiefly to œnanthic ester (ethyl pelargonate), but it varies with the total amount and relative proportions of other volatile constituents present. According to Ordonneau, the peculiar fragrant odour of brandy is due to a very small quantity of a terpene which boils at 178°, and which, on oxidation, gives the characteristic flavour to old brandy.

Over 90 p.c. of the brandy imported into the United Kingdom comes from France, the finest grades being *Cognac* and *Armagnac*, so named from the French towns in which they were originally distilled. But little brandy is now distilled in Cognac itself, the greater part being produced on the brandy farms of the surrounding districts. Other brandies of less value commercially are those of the Midi and the districts of Aude, Gard, Hérault, and Pyrenées Occidentales, commonly known as the 'Trois-six de Montpellier.' Marc brandies are distilled from the fermented 'marc' or refuse of the wine-press as well as from the lees of the wine-casks.

Whilst the term 'Cognac' has by custom come to be used almost as a generic term for 'brandy,' it is, strictly speaking, applicable only to spirits made from wine grown in the Cognac region, which comprises a certain part of the two departments of Charente and Charente Inférieure, also Dordogne and Les Deux-Sévres. A strict delimitation of the Cognac area has been made by the French Government by decree dated 1st May, 1909, and the region is locally subdivided into the Grande or Fine Champagne, the Petite Champagne, the Borderies and the Bois, according to the quality of the wine produced.

The soil of the district is mainly calcareous, and the grape is a small white berry with very acid juice, producing a wine of inferior quality for drinking purposes. (For the extraction and fermentation of the grape juice, *see* WINE.)

As the reputation of the brandies of the Cognac and Armagnac districts depends so much upon their bouquet, they are submitted to slight rectification only, and distillation is therefore usually conducted in a simple 'pot' still by the professional distiller as well as by the farmer. The still, which varies in content from about 150 to 200 gallons, is usually enclosed in brickwork, with only a small bulbous head exposed, and is generally heated by means of a furnace, wood being considered the best fuel. In a few distilleries the stills are heated by steam. Occasionally, a subsidiary vessel, filled with wine and called a 'chauffe-vin,' is attached to the still, and through it the pipe conveying the spirit vapour to the refrigerator passes, heating the wine so that the latter is quickly raised to boiling-point when subsequently passed into the still, thereby effecting a saving of fuel. Two distillations are made, termed 'brouillis' and 'bonne-chauffe,' corresponding respectively with the 'low wines' and 'spirits' of the whiskey distiller.

In some distilleries the finished spirit is produced at one continuous distillation by means of a still described as 'à premier jet.' In this form of still, a vessel is attached to and above the head of the still, and through it the spirit of the first distillation is conveyed. This spirit is again vapourised by the heat of the spirit vapour rising from the still itself on its way to the refrigerator. The spirit produced in this way is not considered so fine as that obtained by the pot still, but it is of higher strength and more suitable for the manufacture of liqueurs.

The quality of the spirit depends greatly on the care with which the distillation process is carried out. The stills should be worked slowly and regularly, the normal time for the complete distillation of a charge being about ten hours.

The quantity of wine used in the process of manufacture is relatively very great, the amount of brandy produced from a given measure being only from 10 to 15 p.c. The strength of the wine varies from 4·5 to 9 p.c. by weight of pure alcohol, or approximately from 10 to 20 p.c. of proof spirit, the average being 6·5 p.c. of alcohol, or 14 p.c. of proof spirit. The finished spirit as run from the still contains about 64 p.c by weight of alcohol, equivalent to a strength of about 25 over-proof. The brandy, as received from the farmers, is blended and diluted in vats, sweetened with cane sugar, slightly coloured with caramel, and filtered (if necessary) into storage vats in which it is matured.

The French Government has by various laws and decrees of the years 1905 to 1909 prohibited the description 'Cognac' to be applied to any mixture of Cognac or other wine spirit, with grain or beet spirit, and has further provided that labels, marks, &c., bearing the word 'Cognac' should signify that the spirit in question is solely the product of the Cognac region (*vide supra*).

The simple pot stills and the modified stills known as 'à premier jet,' above referred to, as being used in the Charente districts, are not suitable for wines having a strong earthy flavour ('terroir') or other undesirable qualities. In such cases, as in the brandies of the Midi, the Rochelle district, and the marc brandies of Burgundy, stills of a more complicated nature are employed, owing to the necessity for a greater degree of rectification. In these the distillation is continuous, and in the Rochelle district and the islands of the N.W. coast, a pot still with a rectifying head, known as the 'Alembic des Iles,' is employed, whilst in the south the distilling column consists of a series of compartments separated by plates or 'plateaux,' connected with taps by means of which it is possible to take off the spirit at a higher or lower strength as desired. These stills are generally heated by direct fire.

Immense quantities of wine are produced in the Midi for conversion into brandy, the grapes of this region being unsuitable for making good wine. This is attributed to the effects of the *Phylloxera*, which devastated the whole of the Charente district in the years 1875–1878. Before this time, most of the brandy exported to the United Kingdom was genuine Cognac, but the destruction of the Charente vineyards stimulated the production of brandy in other parts of France as well as in other countries. The vineyards of the Cognac district were replanted with American stocks, on which Charente vines were grafted, and the result has been highly successful; but in the south of France the vineyards ravaged by the phylloxera were replanted with vines which were not appropriate to the soil, and which yielded wine in great quantity but at the sacrifice of good quality. Hence the use of the rectifying stills in the Midi and the large quantity of brandy produced. Most of this is consumed in France. The spirit derived from diseased or unsound wines is highly rectified and used for industrial purposes. The cheapness of wine, therefore, affords little or no inducement to the distillers of the Midi to use beet or grain as the raw material for the production of their brandies.

The relative values of the spirits above mentioned may be gathered from the average prices per proof gallon in 1909, which just before the war (1914) were from 7*s.* 6*d.* for brandy of the best Cognac district (Champagne) to 3*s.* for Bois brandy, the cheapest in the Cognac district, whilst Midi brandy was 2*s.*, and grain and beet spirit about 1*s.* 3*d.* (f. o. b.) per proof gallon.

Marc brandies or *eaux-de-vie de marc* are, as the name implies, derived from the marc or refuse of the grapes after the juice has been extracted. They have a strong earthy flavour, and usually are very rich in secondary products. They are therefore often added to other wine spirits to impart the brandy character, or admixed with neutral spirit from grain, beet, &c., in the preparation of fictitious brandies.

Algerian brandy is of high quality, resembling Cognac, and is generally sent to France, whence considerable quantities are reshipped from the Charente district to the United Kingdom.

Brandies are produced in most other wine-growing countries, especially when, owing to over-production of wine, or some defect in its quality, it becomes more profitable to convert it into spirit than to dispose of it as 'wine.' The most important commercially are from Spain, Egypt, Germany, South Africa, and Australia, but the quantities of these exported to the United Kingdom are small as compared with French brandies.

The Spanish brandies are similar in character to the French, and command a high price. Genuine Egyptian brandy is made from fresh grapes, although the wine grape is not cultivated in Egypt. The grapes are imported into Alexandria from Southern Turkey, Greece, Cyprus, and Asia Minor, and there made into wine from which the brandy is distilled. They have a strong characteristic flavour, much appreciated by consumers of the cheaper brandies. Spurious brandies of doubtful origin, but described as 'Egyptian,' are also on the market. They are probably made from the currant grape grown in Greece and Asia Minor, and have no right to the title of 'Egyptian,' beyond the fact that they are exported *viâ* Alexandria. Increasing quantities of brandy of fair quality are being produced in South Africa and Australia. The so-called 'dop' brandy of South Africa is produced in the same way as the French 'marc' brandies, and has similar characteristics.

The natural improvement observed in genuine brandies by 'ageing' is always accompanied by a rise in the quantity of the secondary constituents due to the formation of oxidation products (aldehydes and acids) and esters, as well as to concentration due to loss of alcohol and water. The higher alcohols also tend to increase, and furfural to diminish, with age. According to Duplais, the mellowness due to age may be imparted to new brandy, making it fit for immediate use, by adding the following to every 100 litres: old rum, 2·0 litres; old kirsch, 1·75 litres; syrup of raisins, 2·0 litres; and infusion of walnut hulls, 0·75 litre. Low wines which have been kept for some months in casks containing clear rain water preserved by the addition of 10 or 12 p.c. of strong brandy (85°) are also used for a similar purpose.

Whilst there is a legitimate use of colouring which has become practically an essential character of the brandy of commerce, the colour acquired by old brandies, owing to long storage in casks, is often simulated in order to give to new brandies a fictitious appearance of age by means of a tincture of oak extract obtained from chips, shavings, or sawdust of the white oak used at Cognac for making brandy casks.

Brandy was formerly described in the British Pharmacopœia, as 'Spiritus Vini Gallici,' thus implying the French origin of the spirit, and was defined as 'a spirituous liquid distilled from wine and matured by age, and containing not less than 36½ p.c. by weight, or 43½ p.c. by volume of ethyl hydroxide' (approximately 76 p.c. of proof spirit).

This definition, however, takes no cognisance of the nature, quantity, or relative proportions of the secondary products to which the peculiar medicinal properties of brandy are attributed and in view of the variations in these constituents even in the brandies of commerce known to be genuine, and the difficulty of arriving at any satisfactory standard, the British Medical Association eliminated 'brandy' in the last edition of the British Pharmacopœia published in 1914.

The following standards of purity are prescribed by the United States Pharmacopœia. Brandy should be at least 4 years old; its alcoholic content from 39 to 47 p.c. by weight (81–96 p.c. British proof spirit); specific gravity not exceeding 0·941 nor less than 0·925; the residue should not, on the volatilisation of the last traces of alcohol, evolve a marked disagreeable odour of fusel oil, and should not exceed 1·5 p.c.; also the residue from 100 c.c. should dissolve readily in 10 c.c. of cold water, and should be free from more than traces of tannin (*i.e.* should not give more than a pale-green colouration on the addition of a dilute solution of ferric chloride); and the acidity should require not more than 1 c.c. of decinormal alkali for neutralisation using phenolphthaleïn as an indicator.

Under the Sale of Food and Drugs Act, no standard for brandy is fixed beyond the limitation of strength (in common with whiskey and rum) to a minimum of 25 p.c. under proof, below which it may not legally be sold without the fact of dilution being declared. This is now (during the war) superseded by special legislation, which permits of spirits being reduced to a minimum strength of 50 p.c. under proof and 30 p.c. under proof as a maximum strength at which they may be sold as a beverage. The strength of brandy as imported into the United Kingdom varies considerably, but the average is about 5° below proof, or 46·5 p.c. of alcohol by weight.

Ordonneau (Compt. rend. 102, 217) subjected 100 litres of 25-year-old brandy to fractional distillation, and obtained the following substance estimated in grams per hectolitre :—

Aldehyde	3·0
Normal propyl alcohol	40·0
Normal butyl alcohol	218·6
Amyl alcohol	83·8
Hexyl alcohol	0·6
Heptyl alcohol	1·5
Acetic ester	35·0
Propionic, butyric, and caproic esters	3·0
Œnanthic ester (about)	4·0
Acetal and amines	traces

Morin (Compt. rend. 105, 1019) distilled 92 litres of pure cognac in Claudin and Morin's apparatus. The first portion of the distillate contained the more volatile bodies; the second consisted of tolerably pure ethyl alcohol; the third, the higher-boiling alcohols, &c. The residue, chiefly water, was tested for free acids, *iso*butylglycol and glycerol.

The first three portions were then fractionated, 5 litres of light alcohol, 55 litres of pure ethyl alcohol, and 3·5 litres of higher-boiling compounds being obtained. The latter fraction smelt strongly of fusel oil, and possessed a burning taste. The water remaining behind was added to that already obtained. The fractions were then redistilled in Le Bel and Henninger's apparatus. The fusel oil portion, which after dehydration by potassium carbonate weighed 352 grams, gave:

	grams
Water	7
Ethyl alcohol	130
Normal propyl alcohol	25
*Iso*butyl alcohol	6
Amyl alcohol	175
Furfural	2
Wine oils	7

The water contained a little acetic and butyric acids, and a small quantity of a viscous liquid which distilled undecomposed under diminished pressure, and appeared to consist of *iso*butyl alcohol and glycerol. The residue contained tannin, together with substances extracted from the wood.

In the following table: 1 shows the compounds contained in 100 litres of the cognac; 2 shows the same obtained by the fermentation of 100 kilos. of sugar :—

	1 grams	2 grams
Aldehyde	trace	trace
Ethyl alcohol	50,837·00	50,615·0
Norm. propyl alcohol	27·17	2·0
*Iso*butyl alcohol	6·52	1·5
Amyl alcohol	190·21	51·0
Furfural bases	2·19	—
Wine oil	7·61	2·0
Acetic acid	trace	—
Butyric acid	trace	—
*Iso*butyl glycol	2·19	—
Glycerol	4·38	—

Butyl alcohol was absent; furfural was detected directly by the addition of aniline to the cognac, a red colouration being produced in the presence of acetic acid. It will be observed that *iso*butyl alcohol is present only in small quantity, whilst in Ordonneau's results it is absent altogether.

The analytical data usually relied upon for discriminating between genuine brandies and those blended with neutral spirit are (*a*) volatile acids; (*b*) aldehydes; (*c*) esters; (*d*) higher alcohols; and (*e*) furfural. The results are calculated in parts per 100,000 of absolute alcohol, *e.g.* in milligrams per 100 c.c., or grams per hectolitre. The total amount of the secondary products expressed in this manner is termed the 'coefficient of impurities,' or preferably the 'coefficient non-alcohol.' The standard coefficient suggested by Girard and Cuniasse for genuine brandy is 300, of which not less than 80 should be esters. In calculating the proportion of neutral spirit in a mixture, allowance should be made for the small amount of secondary products present in neutral spirit. The average coefficient for industrial alcohol, as shown by the analyses of Girard and Cuniasse, is 17 and the esters 8.

(For a detailed description of the methods of analysis employed, *see* Thorpe, Minutes of Evidence taken by the Royal Commission on Whiskey and other Potable Spirits, ii. Appendix Q, xii. 1909.)

The causes which affect the characteristic bouquet of the wine naturally influence the proportion as well as the character of the volatile matters included in the 'coefficient' of the brandy. Thus the proportion of acids and esters is considerably augmented if the wine becomes sour, and, speaking generally, the aldehydes are higher in white than in red wines. Also in regard to distillation, the aldehyde and more volatile esters are found mainly in the first runnings ('produits de tête'), whilst the higher alcohols and furfural occur in largest quantity in the tailings ('produits de queue').

In the brandies of Charente and Armagnac the coefficient is usually rather high, but ordinarily, in cognacs and *fine champagne*, it ranges between 275 and 450, although occasionally it falls considerably beyond these limits. Brandies obtained from wines of the Midi and from Algeria show much wider variations, ranging from 25 (indicating strong rectification) to 500. Marc brandies have almost invariably a very high coefficient, ranging from 500 to nearly 1500, and in these, aldehydes often form a large proportion.

Attempts have been made to fix minimum and maximum values for the coefficient, but without much success, the former with a view to the detection of the admixture of neutral spirit, and the latter to restrict the amount of secondary products for hygienic reasons. The effect of such limits would be to condemn many brandies that are undoubtedly genuine and even of high commercial value.

From the hygienic point of view, the esters, furfural, and especially the aldehydes, have a much more deleterious action on the human system than the higher alcohols, whilst the acids, particularly acetic, which frequently forms a large proportion of the coefficient, cannot be said to have any detrimental influence.

The French Government, in 1904, instituted an inquiry by the Technical Committee of Œnology into the possibility of fixing standards for the total amount of secondary products ('coefficient non-alcohol') of genuine brandy, but the conclusion arrived at was that neither a minimum nor a maximum limit could be recommended owing to the extremely variable character of brandy, not only with respect to the coefficient as a whole, but also in regard to the proportions of the volatile constituents relatively to each other. Chemical analysis should not be relied upon alone, but should be supplemented and its results confirmed by expert tasting ('degustation').

British brandy is usually made from grain spirit distilled with certain flavouring materials, or by adding flavouring ingredients to the spirits. It is frequently mixed with foreign brandy, and is largely used for cooking purposes.

Amongst the flavouring ingredients used in the manufacture of artificial brandies (including British brandy) may be mentioned the following: œnanthic ester, tincture of catechu, balsam of tolu, acetic ester, argol, cognac oil, essence of cognac, infusions of bitter almond shells, tea, and walnut hulls, liquorice root, prune juice, rum, syrup of raisins, vanilla, &c. So-called 'cognac essences' contain mixtures of the aromatic compounds just mentioned, whilst 'cognac oil' is made by the distillation of a mixture of alcohol, coco-nut oil, and sulphuric acid, œnanthic ester being one of the products.

Cider brandy is manufactured in the United States and Canada from cider and perry.

Danzig brandy is made from rye ground with the root of *Calamus aromaticus*.

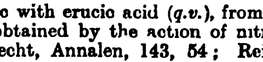
Guernsey brandy is the spirit of beet root flavoured to imitate true brandy.

Hamburg brandy is said to consist of potato or beet-root spirit as a basis, flavoured with essences or by the addition of inferior brandy, and coloured to represent genuine brandy. Similar imitation brandies appear to be made in the north of France, in Belgium, and in other foreign countries. (Girard and Cuniasse, Man. pratique de l'Analyse des Alcools et des Spiritueux; Schidrowitz, Analyst, June, 1905, and June, 1906; Thorpe, Nature, 3 Nov. 1904; and Report of Royal Commission on Whiskey and other Potable Spirits, 1908–9.) J. C.

BRASS *v.* Zinc.

BRASSIC ACID *v.* Brassidic acid.

BRASSIDIC ACID (*Brassic acid*)



$$\begin{matrix}H\\C_8H_{17}\end{matrix}\!\!>C:C<\!\!\begin{matrix}H\\C_{11}H_{22}\cdot CO_2H\end{matrix}$$

is isomeric with erucic acid (*q.v.*), from which it may be obtained by the action of nitrous acid (Hausknecht, Annalen, 143, 54; Reimer and Will, Ber. 1886, 3321; Websky, Jahrb. Chem. 1853, 444; Fitz, Ber. 1871, 444); by treatment with hydrogen bromide in acetic acid solution, monobrombehenic acid $C_{22}H_{42}O_2Br$, being also formed (Ponzio, Gazz. chim. ital. 35, ii. 394); and by heating with concentrated sulphurous acid at 200° (M. K. and A. Saytzew, J. Russ. Phys. Chem. Soc. 24, 482; J. pr. Chem. 50, [2] 78). It may also be obtained by heating behenolic acid with zinc and acetic acid, and a few drops of hydrochloric acid (Holt. Ber. 1982, 962), and by the reduction of monobrombrassidic acid, which is obtained by treating behenolic acid with hydrogen bromide (Hasse and Stutzer, Ber. 1903, 3601). Brassidic acid crystallises from alcohol in plates, m.p. 65°–66° (Saytzew, *l.c.*), b.p. 282° (30 mm.), 265° (15 mm.), 256° (10 mm.), 180° (0 mm.), (Krafft and Weilandt, Ber. 1896, 1325); sp.gr. 0·8585 at 57·1°/4°; is less soluble than erucic acid in alcohol and ether. (For relationship to erucic acid and comparison of their behaviour towards various reagents, *v.* Albitzky, J. Russ. Phys. Chem. Soc. 31, 76; 34, 788; J. pr. Chem. 61, [2–3] 65; Mascarelli, Atti. R. Accad. Lincei, 1917, [v.] 26, i. 71). By fusing brassic acid with potash, *arachidic acid* $C_{20}H_{40}O_2$ is obtained (Goldschmidt, Jahrb. Chem. 1877, 728); oxidation with potassium permanganate yields a dihydroxybehenic acid (Jukovsky, J. Russ. Phys. Chem. Soc. 24, 499; Albitzky, *l.c.*). Treatment with hydriodic acid in glacial acetic acid yields iodobehenic acid (Bayer and Co., D. R. P. 180087; Chem. Soc. Abst. 1907, i. 380).

BRASSIL. A local name for iron pyrites.

BRASSYLIC ACID $C_{13}H_{24}O_4$. Obtained, together with other products, by acting on behenolic acid $C_{22}H_{40}O_2$, with fuming nitric acid (Hausknecht, Annalen, 143, 45; Grossmann, Ber. 1893, 644) May be prepared by the action of nitric acid on erucic acid (Fileti and Ponzio, Gazz. chim. ital. 23, ii. 393), and from ικ-undecenoic acid (Krafft and Seldis, Ber. 1900, 3571). Flat needles; m.p. 113°–114°; readily soluble in alcohol and ether, sparingly soluble in water.

BRAUNITE. A manganese mineral classed with the oxides, but containing an appreciable amount of silica (8–10 p.c.), the formula being $3Mn_2O_3\cdot MnSiO_3$ or $4Mn_2O_3\cdot MnSiO_3$. The manganese is usually isomorphously replaced by small amounts of iron, calcium, barium, &c. It is generally found in compact masses, but sometimes as tetragonal pyramids, the angles of which are very near to those of the regular octahedron. The crystals possess a perfect pyramidal cleavage. The colour is black with a sub-metallic to metallic lustre. Sp.gr. 4·8; H. 6–6½. The mineral i found in the manganese-mines in Sweden; and with the exception of psilomelane, it is the mos abundant of the manganese ores in India (L. L. Fermor, Mem. Geol. Survey, India, 1909 xxvii). L. J. S.

BRAZILITE. A synonym of baddeleyite (*q.v.*). The same name has also been applied to an oil-bearing rock from Bahia, Brazil. L. J. S.

BRAZIL NUTS are the fruits of *Bertholletia excelsa* (Humb. and Bonp.). They yield 73 p.c. of a fatty oil of pale yellow colour, of a taste similar to that of the nuts themselves. In South America an edible oil is expressed from the fresh nuts, but the oil known in Europe is derived from mouldy nuts, and is only fit for the manufacture of soap. The oil deposits a large amount of 'stearine' on standing. It is a 'semi-drying' oil; iodine value about 106; m.p. of fatty acids 28°–30° (De Negri and Fabris). J. L.

BRAZILETTO. An inferior kind of Brazil-wood obtained from *Cæsalpinia braziliensis* (Linn.), growing in th West Indies.

BRAZILWOOD. Under the name of Brazilwood certain varieties of the so-called 'soluble' red woods are known, the term 'soluble' being employed to distinguish them from the dyestuffs of the barwood class, which only with difficulty yield their colouring matters to boiling water. These soluble red woods give with aluminium mordanted fabrics, a bright-red shade, which in each case is derived from one and the same colouring matter, and all are botanically allied, in that they consist of the wood of various species of *Cæsalpinia*. About nine varieties have been employed as dyestuffs, of which the following are the best known:—

Fernambuco or *Pernambuco wood* is considered to be the richest in colouring matter, and is the product of the *Cæsalpinia crista*, a tree which is abundant in Jamaica and Brazil.

The true *Brazilwood* is derived from the *Cæsalpinia braziliensis*, and is said to contain only one-half the colouring matter which is present in the Fernambuco variety. It is obtained exclusively from Brazil.

Sappanwood is obtained from the *Cæsalpinia sappan*, a tree which is common to the warmer regions of Asia. The so-called *Limawood* is a variety of sappan, and the dyewood imported from the Philippine Islands is an inferior quality of this product.

Peachwood is the product of the *Cæsalpinia echinata*, which occurs in Central America and the northern parts of South America.

These woods, which are very hard, and of a deep-red colour, come into the market in the form of billets varying in weight from a few pounds up to a hundredweight. If freshly cut, the internal colour of the wood is seen to be light-yellow, but this soon changes to deep-red in contact with air.

Some varieties of these woods were employed for dyeing purposes in India long before the discovery of America, and it is stated that when South America was discovered by the Spaniards, in 1500, the northerly portion of the country was named Brazil (from *braza*, fiery red), because this red dyewood was found there in such immense quantities.

Owing to the fugitive character of the colours yielded by Brazilwood, it is now only employed to a somewhat limited extent.

Brazilin $C_{16}H_{14}O_5$, the colouring principle of Brazilwood, was first isolated in a crystalline condition by Chevreul (Ann. Chim. Phys. [1] 66, 225); but was not further examined until 1864, when Bolley (Schweiz. polv. Zeitsch. ix. 267) assigned to it the formula $C_{22}H_{20}O_7$ Subsequently Kopp (Ber. 6, 446) proposed the formula $C_{22}H_{18}O_7$, but it was left to Liebermann and Burg (Ber. 9, 1883) to determine the exact composition of this substance, and their formula, $C_{16}H_{14}O_5$, is in use at the present time. To prepare brazilin from the wood itself, it is best to employ the commercial extract. This is stirred up with a considerable quantity of sand, the product extracted with cold ether, the ethereal liquid evaporated to a small bulk, treated with a little water, and allowed to stand for some days. Crystals slowly separate, and these are purified by crystallisation from a little water.

This method is, however, tedious, and the usual source of brazilin consists of the crude crystalline crusts of this substance which are frequently deposited from Brazilwood liquor, and intermediate product in the manufacture of Brazilwood extract. The crude substance is best purified by two or three crystallisations from water, to which a little sulphurous acid has been added (Gilbody, W. H. Perkin, and Yates, Chem. Soc. Trans. 1901, 79, 1396). Brazilin crystallises in two forms, either as colourless needles containing $1\frac{1}{2}H_2O$, or as colourless prisms with $1H_2O$. It is readily soluble in alcohol and water, and dissolves in a dilute solution of sodium carbonate with a beautiful carmine-red colour.

Tetraacetylbrazilin $C_{16}H_{10}O_5(C_2H_3O)_4$, colourless needles, m.p. 149°–151° (Liebermann and Burg); *triacetylbrazilin* $C_{16}H_{11}O_5(C_2H_3O)_3$, needles, m.p. 105°–106° (Buchka and Erck, Ber. 18, 1139); *brombrazilin* $C_{16}H_{13}BrO_5$, brown-red leaflets (B. and E.); *dibrombrazilin* $C_{16}H_{12}Br_2O_5$, leaflets (Schall and Dralle, Ber. 23, 1550); *tetraacetylbrombrazilin* $C_{16}H_8Br_2O_5(C_2H_3O)_4$, needles, m.p. 203°–204° (Buchka, Annalen, 17, 685); *tetraacetyldibrombrazilin* $C_{16}H_6Br_2O_5(C_2H_3O)_4$, m.p. 185° (S. and D.); *tribrombrazilin* $C_{16}H_{11}Br_3O_5$ (S. and D); *dichlorbrazilin* $C_{16}H_{12}Cl_2O_5$ (L. and B.); and *tetrabrombrazilin* $C_{16}H_{10}Br_4O_5$, fine red needles (B. and E) have been prepared.

When brazilin is methylated with methyl iodide in the usual manner, it gives *brazilin trimethyl ether* (S. and D., Ber. 20, 3365; Herzig, Monatsh. 14, 56; and Schall, Ber. 27, 525) $C_{16}H_{11}O_2(OCH_3)_3$, prisms, m.p. 138°–139°, which on acetylation yields *acetylbrazilin trimethyl ether* $C_{16}H_{10}O_2(OCH_3)_3(C_2H_3O)$, m.p. 171°–173° (Herzig, Monatsh. 15, 140; Schall, Ber. 27, 236).

According to Gilbody, W. H. Perkin, and Yates (Chem. Soc. Trans. 79, 1403), large quantities of the trimethyl ether are conveniently prepared as follows: 143 grams of brazilin dissolved in the smallest possible quantity of methyl alcohol are treated with 35 grams of sodium in methyl alcohol and methyl iodide (250 grams), and the mixture is heated 50 hours to 60°–65° in absence of air. A second method employed also by v. Kostanecki and Lampe (Ber. 35, 1669) consists in methylating brazilin with excess of dimethyl sulphate and alkali.

The difficulty experienced in fully methylating brazilin is evidence of the presence of an alcoholic group; but the *tetramethyl ether* $C_{16}H_{10}O(OCH_3)_4$, m.p. 137°–139°, has been prepared by Schall by treating the sodium compound of the trimethyl derivative suspended in benzene with methyl iodide at 120° (compare also Herzig, *l.c.*). From this substance the following derivatives have been prepared:—

Brombrazilin tetramethyl ether $C_{16}H_9BrO\cdot(OCH_3)_4$, prisms, m.p. 180°–181° (S. and D., Ber. 21, 3014); and *dibrombrazilin tetramethyl ether* $C_{16}H_8Br_2O\cdot(OCH_3)_4$, m.p. 215° (S and D. Ber 23, 1432).

When brazilin is submitted to dry distillation, it gives *resorcin* (Kopp, *l.c.*), and by fusing it with potassium hydroxide, Liebermann and Burg obtained resorcin, and Herzig (Monatsh. 27, 739) also *protocatechuic acid*. With nitric acid brazilin yields *trinitroresorcinol* (Reim, Ber. 4, 334).

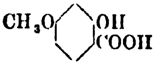
When brazilin, the colouring principle, is oxidised under suitable conditions, it is converted into *brazilein*, the true colouring matter

$$C_{16}H_{14}O_5+O=C_{16}H_{12}O_5+H_2O$$

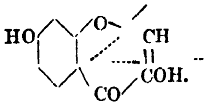
and for this purpose the action of air on an alkaline brazilin solution, alcoholic iodine (Liebermann and Burg), potassium nitrite, and acetic acid (Schall and Dralle), nitric acid in the presence of ether (Buchka and Erck), and sodium iodate (Mayer, Zentr. 1904, i. 228) have been employed. It can, however, be more economically prepared from Brazilwood extract in the following manner (Hummel and A. G. Perkin, Chem. Soc. Trans. 1882, 41, 367):—

To an aqueous solution of the extract of the wood, an excess of ammonia is added, and air is aspirated through the liquid. A precipitate of the impure ammonium salt of brazilien gradually separates, and this is collected, dissolved in hot water, and treated with dilute acetic acid (sp.gr. 1·04). A brown viscous precipitate of the crude colouring matter is thus obtained, which is extracted with hot dilute acetic acid, and the extract evaporated on the water-bath. Crystals of brazilein separate, which are collected and washed with acetic acid.

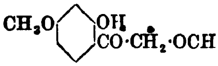
Brazilein consists of minute plates possessing a strong metallic lustre, and by transmitted light a reddish-brown colour. It is very sparingly soluble in all the usual solvents, and cannot be recrystallised in the ordinary manner. It is in reality the colouring matter of Brazilwood, and possesses strong tinctorial property. Alkaline solutions dissolve it with a deep-red colouration, which on standing in air passes gradually to brown. A study of this oxidation was carried out by Schall and Dralle, with interesting results. 2·7 grams of brazilin dissolved in 150 c.c. of water was treated with 10 c.c. of sodium hydroxide solution (sp gr. 1·37), and air aspirated through the liquid for 36 hours. Ether extracted from the acidified solution *β-resorcylic acid*, and a substance $C_9H_6O_4$, crystallising in brownish-yellow needles, m.p 271°, which gave a *diacetyl* compound, m.p 148°-149°, and a *dimethyl* ether, m.p. 169°-170°. When the latter was oxidised in acetic acid solution, with potassium permanganate *β-resorcylic acid monomethyl ether* was produced :



Schall and Drallo considered that this compound was probably a pheno-γ-pyrone derivative, and Feuerstein and Kostanecki (Ber. 32, 1024) proved that this was in reality the case, and assigned to it the following constitution :—



Thus the dimethyl ether, when hydrolysed with alcoholic potash, gave *fisetol dimethyl ether*

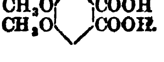


a substance which had already been obtained in a similar manner by Herzig from fisetin tetramethyl ether (*see* Young Fustic).

Our chief knowledge of the constitution of brazilin is due to the elaborate investigations of W. H. Perkin and his pupils, who obtained most important results by the oxidation of brazilin trimethyl ether with potassium permanganate, and also with chromic acid.

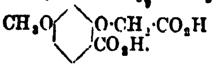
Gilbody, Perkin and Yates (Chem. Soc. Trans. 1901, 79, 1465) found that when brazilin trimethyl ether is oxidised with permanganate, it gives, in addition to oxalic, acetic, and formic acids, the following compounds :—

1. *m-Hemipinic acid*

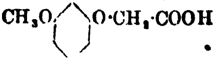


The isolation of this substance was important, since it showed that brazilin contains a catechol nucleus and two orthohydroxyls, and as a result of these latter no doubt in part its tinctorial properties are due.

2. 2 *Carboxy-5-methoxyphenoxyacetic acid*

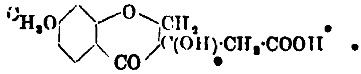


On fusion with alkali, this compound yields resorcinol, and on heating with water to 200° is converted into *methoxyphenoxyacetic acid*

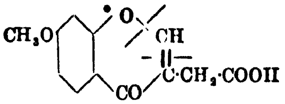


This can be synthesised by the interaction of ethylbromacetate and the sodium compound of resorcinol monomethyl ether and subsequent hydrolysis.

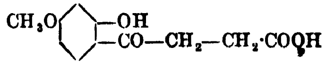
3. *Brazilic acid*



when fused with alkali, gives resorcin, and on warming with sulphuric acid is converted into *anhydrobrazilic acid*

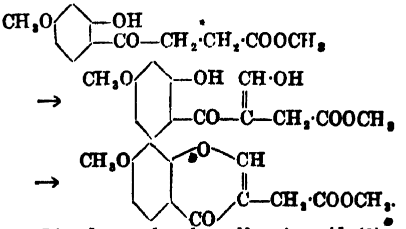


Boiling baryta water hydrolyses anhydrobrazilic acid, with production of *formic acid* and 6-*hydroxy*-4-*methoxybenzoylpropionic acid*

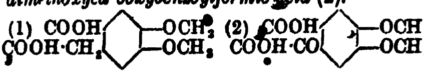


On methylation this is converted into the dimethyl ether, and the latter can be produced by the interaction of dimethyl resorcinol and the half-chloride of succinic acid monoethyl ester, and subsequent hydrolysis. It is also formed when resorcinol dimethyl ether and succinic acid are treated with aluminium chloride without employing a solvent.

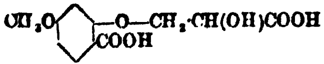
Finally, when the methyl ester of this hydroxymethoxybenzoylpropionic acid is dissolved in ethyl formate and treated with sodium, the *methyl ester* of *anhydrobrazilic acid* is produced. This interesting synthesis may be represented as follows :—



Dimethoxycarboxybenzylformic acid (1), and *dimethoxycarboxybenzoylformic acid* (2).

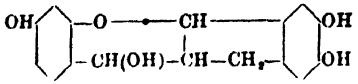


represent intermediate stages in the formation of *m*-hemipinic acid from brazilin trimethyl ether, whereas the acid



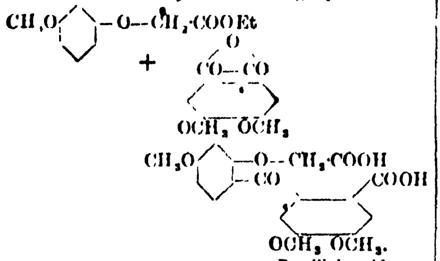
also isolated, is, no doubt, that product of the oxidation which is anterior to the formation of carboxymethoxyphenoxyacetic acid (*see* above)

The earlier work suggested the following probable constitution for brazilin :—



but this, as a result of the investigation of brazilinic acid, a very important substance, also produced by the oxidation of brazilin trimethyl ether, was subsequently discarded.

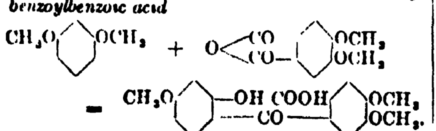
Brazilinic acid. The constitution of this acid has been conclusively demonstrated by its synthesis, which has been effected by the interaction of *m*-hemipinic anhydride with ethyl methoxyphenoxyacetate in the presence of aluminium chloride. This is illustrated by the following equation.—



Brazilinic acid.

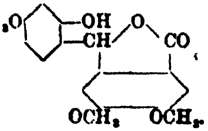
When brazilinic acid is reduced with sodium amalgam, it is quantitatively converted into *dihydrobrazilinic acid* $C_{19}H_{20}O_9$, which at once loses water with the formation of the *lactone* $C_{19}H_{18}O_8$.

To synthesise the latter compound, *m*-hemipinic anhydride is condensed with resorcinol dimethyl ether to form *2-hydroxy-4.5'.4'-trimethoxy benzoylbenzoic acid*

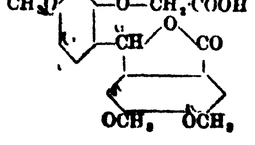


When reduced with sodium amalgam, this acid gives *2-m-meconyl-5-methoxyphenol* (1), and this by the action of chloracetic acid and potassium hydroxide is converted into the lactone of dihydrobrazilinic acid (2)

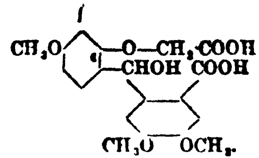
(1)



(2)

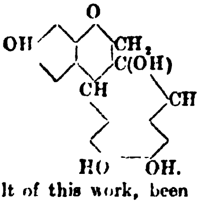


(3)



Dihydrobrazilinic acid itself is accordingly represented by formula (3).

The following constitution :—



has, as a result of this work, been assigned to brazilin by Perkin and Robinson (Chem. Soc. Trans. 1908, 93, 496), and is in complete harmony with the facts above enumerated.

Oxidation of trimethylbrazilin with chromic acid

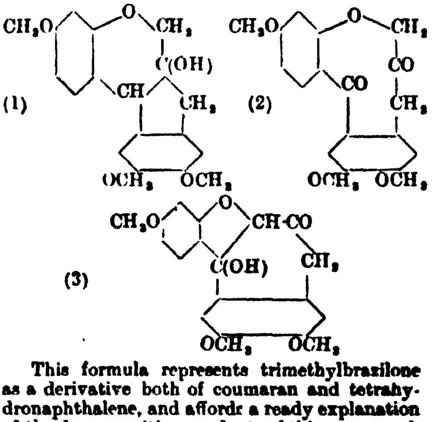
When trimethylbrazilin is oxidised with chromic acid it is converted into *trimethylbrazilone* (Gilbody and Perkin, *v. infra*)—

$$(CH_3O)_3C_{16}H_{11}O_2 + 2O = (CH_3O)_3C_{16}H_9O_3 + H_2O$$

and this apparently simple reaction has proved to be of an extremely puzzling character.

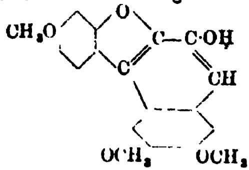
When trimethylbrazilone is oxidised with permanganate, it gives *m-hemipinic acid, 2-carboxy-5-methoxyphenoxyacetic acid, brazilic acid, dimethoxycarboxybenzoylformic acid, dimethoxycarboxybenzylformic acid, methoxycarboxyphenoxylactic acid,* and *brazilinic acid.*

In an earlier paper, Gilbody and Perkin (Chem. Soc. Trans 1902, 81, 1040) suggested for trimethylbrazilone a constitution based upon their first formula for brazilin (*see* above), but it was subsequently shown (*ibid* 1908, 93, 498) that the reaction proceeds as follows · By the oxidation of trimethylbrazilin (1) with chromic acid a disruption of the central linkage occurs, with the formation of an unstable diketone (2), and this subsequently undergoes aldol condensation, and trimethylbrazilone is produced (3)—



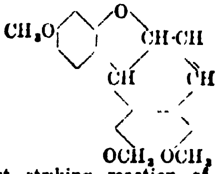
This formula represents trimethylbrazilone as a derivative both of coumaran and tetrahydronaphthalene, and affords a ready explanation of the decomposition products of this compound.

An important point in favour of this constitution is afforded by the behaviour of trimethylbrazilone with alkalis, or acetic anhydride and other dehydrating agents, for it is thus converted with loss of one molecule of water into *anhydrotrimethylbrazilone* $(CH_3O)_3C_{16}H_7O_2$. There can be little doubt that the formation of this substance is due to the elimination of water from the aldol grouping in trimethylbrazilone, and that it possesses the following formula:



Anhydrotrimethylbrazilone is thus a derivative of *β-naphthol*, and it possesses many of the properties of this substance. It is soluble in dilute alkali, and this solution gives with diazobenzene chloride a red azo- dyestuff. Diazonaphthalene chloride behaves similarly, and the dye thus produced dissolves in sulphuric acid with a blue colour.

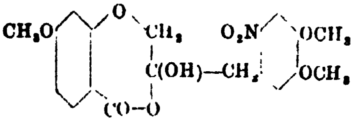
When trimethylbrazilone is boiled in acetic acid solution with phenylhydrazine, *deoxytrimethylbrazilone* $C_{16}H_9O_2(CH_3O)_3$ is obtained, and this is probably a dihydronaphthalene derivative of the formula



The most striking reaction of trimethylbrazilone is its behaviour with nitric acid, when it yields a compound possessing the composition of a *nitrohydroxydihydrotrimethylbrazilone*

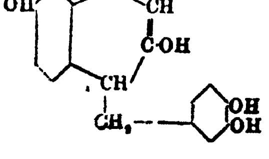
$$C_{16}H_9O_2(CH_3O)_3+HNO_3 = C_{16}H_{10}O_6N(CH_3O)_3$$

This substance dissolves in alkali with a purple colour, but on standing the colour rapidly fades, *o-nitrohomoveratrol* separates, and the solution contains *p-methoxysalicylic acid.* Oxidation with permanganate gives *2-carboxy-5-methoxyphenoxyacetic acid*, and these decompositions point clearly to the formula



as representing the constitution of this nitro-compound. (*See also* Perkin and Robinson, *ibid.* 1909, 95, 381.)

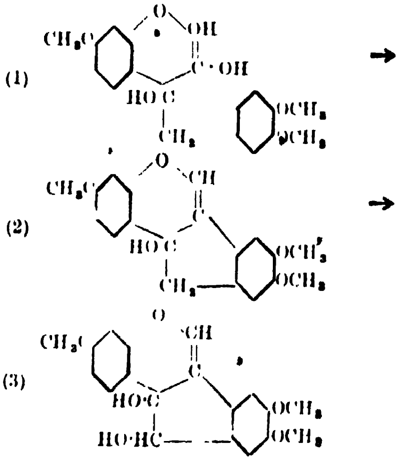
Feuerstein and v. Kostanecki (Ber. 32, 1024) assigned at first the following constitution to brazilin:—



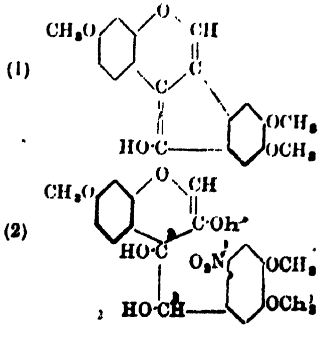
which was based upon the production from it of dihydroxypheno-γ-pyrone (Schall and Dralle) by alkaline oxidation, and of protocatechuic acid by fusion with alkali (Herzig).

It was, however, pointed out by Perkin that this formula does not account for the presence of *m*-hemipinic acid among the oxidation products of trimethylbrazilin, and Herzig and Pollak (Monatsh. 1901, 22, 207) advanced a similar criticism. On the other hand, it was suggested at the time by v. Kostanecki and Lampe (Ber. 1902, 35, 1667) that *m*-hemipinic acid was not to be regarded as an oxidation product of trimethylbrazilin itself, but that it arose from the formation, during the oxidation, of a phenanthrene or indene- derivative, which by the further action of permanganate gives this acid. Such an indene-condensation is illustrated by the following scheme, which, according to these authors, probably occurred during the formation of trimethylbrazilone from trimethylbrazilin.

The first product of the oxidation with chromic acid will possess the formula (1), and this is converted by the following stages into trimethylbrazilone (3).—

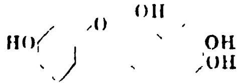


This constitution accounts in a simple manner for the formation of the anhydrotrimethylbrazilone (1), and the nitrohydroxydihydrotrimethylbrazilone (2), of Perkin, which can be represented as follows:—

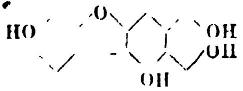


When anhydrotrimethylbrazilone is digested with hydriodic acid, anhydrobrazilone $C_{16}H_{10}O_5 + H_2O$ is produced, but when trimethylbrazilone itself is treated in a similar manner, the result is of a peculiar nature. The compound $C_{16}H_6O(OH)_4$ so obtained does not consist of brazilone, but possesses the formula (1) or (2), and on distillation with zinc dust gives *brazan* (3) (Kostanecki and Lloyd, Ber. 1903, 36, 2193).

1.



2.



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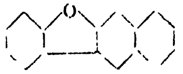
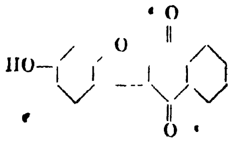
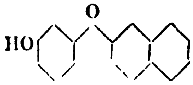


In 1899 Liebermann (Ber. 32, 924) obtained anhydro-*a*-naphthoquinone resorcin by the condensation of 2·3-dichlor-*a*-naphthoquinone with resorcin

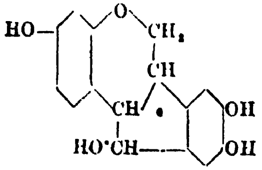


and this, according to v. Kostanecki and Lampe (Ber. 1908, 41, 2373), is 3-hydroxybrazanquinone By reduction with hydriodic acid, this gives hydroxybrazan



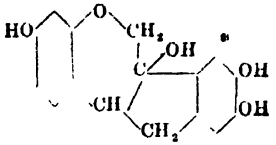
and from this latter or from the quinone itself, brazan, identical with that obtained from trimethylbrazilone, is produced by distillation with zinc-dust. Brazan crystallises in leaflets, and melts at 202°.

v. Kostanecki and Lampe (Ber. 1902, 35, 1674) considered it probable that, after all, trimethylbrazilin does contain, as found by Perkin, a nucleus which on oxidation yields hemipinic acid, and appear to have adopted the following as their final formula for brazilin :—

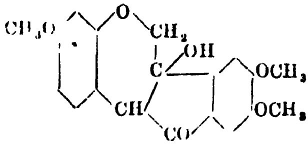


This constitution, it is evident, will still harmonise with the formulæ of trimethylbrazilone and anhydrotrimethylbrazilone given above by these authors.

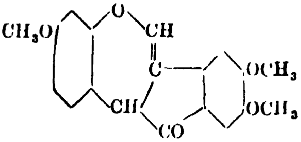
Herzig and Pollak (Ber. 1906, 39, 267) suggested the following constitution for brazilin, trimethylbrazilone, and anhydrotrimethylbrazilone :—



Brazilin.

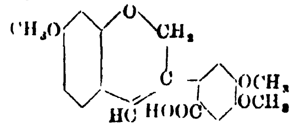


Trimethylbrazilone.

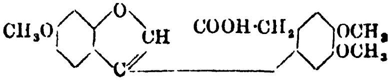


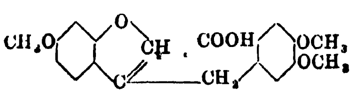
Anhydrotrimethylbrazilone

Herzig, moreover, observed (Ber. 1904, 37, 631) that trimethylbrazilone undergoes isomeric change when it is dissolved in sulphuric acid, and yields *γ-trimethylbrazilone* $C_{16}H_9O_3(OCH_3)_3$, m.p. 170°–173°, to which the formula

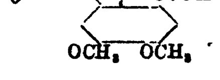


was assigned (Herzig and Pollak, Monatsh. 1906, 27, 743). Perkin and Robinson (*l.c.*) find that on oxidation with permanganate this compound gives large quantities of *2-carboxy-4 5-dimethoxyphenylacetic acid* $(CH_3O)_2{\cdot}C_6H_2{\cdot}(COOH){\cdot}CH_2{\cdot}COOH$, and that there can be little doubt that its true constitution is represented by one of the following formulæ :—





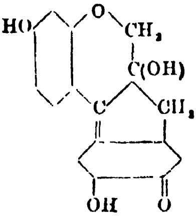
Finally, in 1906 Herzig and Pollak (Monatsh. 27, 743) considered it necessary to modify their first formula for brazilin, and have arrived at the conclusion that that finally proposed by v. Kostanecki and Lampe correctly represents this colouring principle. The more recent work of Perkin and Robinson detailed above shows, however, that such a constitution cannot be correct, because it does not account for the production of brazilinic acid by the oxidation of trimethylbrazilin



and there is every reason to consider that the formula suggested by the latter authors is the correct representation of the constitution (*cf.* also Perkin and Robinson, Chem. Soc. Trans. 1909, 95, 381) of brazilin.

Brazilein yields a triacetyl derivative $C_{16}H_9O_5(C_2H_3O)_3$, yellow leaflets, m.p. 203°-207° (Schall and Dralle, Ber. 23, 1434), and a trimethyl ether $C_{16}H_9(OCH_3)_3O_2$, which crystallises in two modifications, melting at 160° and 178° respectively (Engels and Perkin, Chem. Soc. Proc. 1906, 22, 132). Brazileïn trimethyl ether combines with formic acid, yielding a formic acid derivative which crystallises in garnet-coloured prisms, and is decomposed into its components by treatment with alcohol.

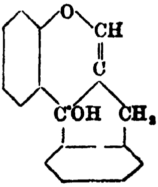
The constitution assigned to brazilein by Perkin is as follows :—



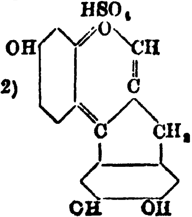
When brazilein is dissolved in sulphuric acid and the solution is diluted with acetic acid, minute orange-red prisms of *isobrazilein sulphate* $C_{16}H_{11}O_4{\cdot}SO_4H$ separate (Hummel and A. G Perkin, Chem. Soc. Trans. 1882, 41, 367), and this, on treatment with alcohol, gives the basic sulphate $C_{16}H_{12}O_5(C_{16}H_{11}O_4{\cdot}SO_4H)_2$, which crystallises in red needles. Hydrochloric and hydrobromic acids at 100° give *isobrazileinchlorhydrin* $C_{16}H_{11}O_4{\cdot}Cl$, and *isobrazileinbromhydrin* $C_{16}H_{11}O_4Br$, and both compounds consist of orange-coloured prisms, which are somewhat readily soluble in water, forming a solution which contains free haloid acid. These interesting substances dye mordanted fabrics colours which are entirely different from those yielded by brazilein, and the shades which are produced, especially on calico, somewhat resemble those given by alizarin. From these haloid salts by digestion with silver oxide a substance is produced known as *isobrazilein*, which has the formula $C_{16}H_{12}O_5$, but is totally distinct from brazilein.

According to Engels, Perkin, and Robinson (Chem. Soc. Trans. 1908, 93, 1140), whose paper must be consulted for the detailed account of brazilein and its derivatives, these *iso*brazilein salts are derived from *4·3-indenobenzopyranol* (1), and the sulphate which is *trihydroxy-4·3-indenobenzopyranolanhydrohydrogen sulphate* (2), may be represented thus :

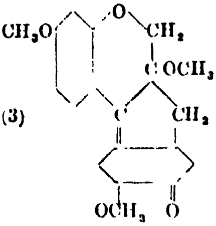
(1)

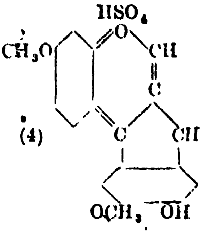


(2)



It was found, for instance, that when brazilein trimethyl ether (3) is treated with sulphuric acid, it is converted with loss of methyl alcohol into the dimethyl ether of *iso*brazilein sulphate (4)

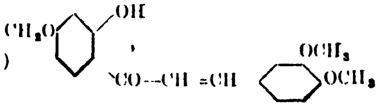




These authors assign an orthoquinonoid structure to this and similar oxonium salts.

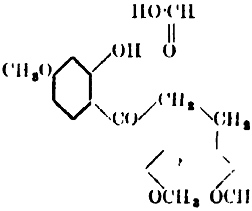
More recently Crabtree, Robinson, and Turner (Chem. Soc. Trans. 1918, 113, 859), employing butein trimethyl ether, have succeeded by very simple methods in synthesising isobrazilein hydrochloride. By reducing butein trimethyl ether (1) :—

(1)

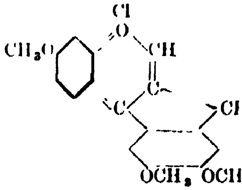


the dihydro (benzylacetophenone) compound (2) is obtained. This by digestion with an excess of absolute formic acid in presence of zinc chloride is transformed into the hydrochloride of isobrazilein trimethyl ether (3) :—

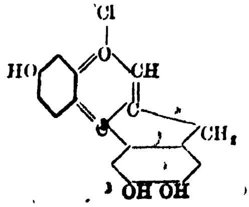
(2)



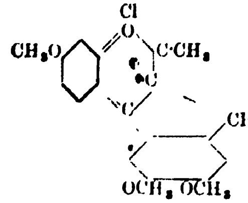
(3)



With fuming hydrochloric acid at 120°-150° demethylation occurs and isobrazilein hydrochloride is produced :—



By the substitution of acetic acid for formic acid in this reaction the corresponding methyl isobrazilein derivative can be obtained :—



The synthesis in this manner of a colouring matter so closely allied to brazilin itself by the employment of butein, a yellow dye which exists in the flowers of the *Butea frondosa* (Perkin, Chem. Soc. Trans. 1904, 85, 1459), is of exceptional interest.

The *commercial preparations* of Brazilwood known as Brazilwood extract and Brazilwood liquor, are prepared by boiling the ground fresh wood with water, and evaporating the decoction thus obtained to various degrees of consistency without access of air, or as rapidly and at as low a temperature as possible, *e.g.* in vacuum pans.

Dyeing Properties.—Before dyeing, the logs as imported are rasped to a coarse powder, and this is then usually moistened with water and allowed to ferment for some weeks. This operation is performed in order to increase the colouring power of the wood, and there can be little doubt that a considerable quantity of the brazilin present is thereby oxidised to the colouring matter brazilein. It has been considered by some that the fresh wood contains in reality a glucoside of brazilin, which, under the influence of fermentation, is hydrolysed, but no evidence has been forthcoming in support of this suggestion.

Although still used in calico-printing and in wool-dyeing, Brazilwood and its allies have lost their importance, chiefly because of the fugitive character of the colours they yield. In calico-printing, sappan liquor is employed for producing steam-reds and pinks, the mordant used being aluminium acetate or stannic oxalate, separately or combined, together with some oxidising agent, *e.g.* potassium chlorate or a copper salt. It also enters into the composition of steam-chocolates and certain steam colours in conjunction with other dyewood extracts. These woods have also been much used in the past along with garancine in dyeing the reds, chocolates, and other colours of cheap prints.

In wool-dyeing these woods have been applied for the purpose of dyeing reds and various shades of claret and brown, the wool being previously mordanted with alum and cream of tartar or oxalic acid, or with potassium dichromate, in which case other dyewoods, *e.g.* logwood and old fustic, are applied in addition. The colours produced by this method are now only used to a limited extent.

In cotton-dyeing, peachwood-red was formerly obtained by first preparing the cotton with tannin matter, then mordanting with a stannic salt, and finally dyeing with peachwood, sappanwood, &c. Browns were obtained by the use of logwood in addition, with or without a final passage through a ferric salt solution (nitrate of iron). These colours are now replaced by others obtained from coal tar. A. G. P.

BRAZILEIN and **BRAZILIN** *v.* BRAZILWOOD.

BRAZILIAN ANIME *v.* OLEO-RESINS.

BREAD may be defined as the dough made by the mixture of the flour of grain with water, charged in some way with gas so as to distend it, and afterwards baked. The resulting loaf has a delicate spongy structure which causes it to be the most readily and easily digested of all wheat foods. The simplest and most primitive form of bread making consisted merely in mixing flour with water and baking the dough, and it survives still in the Passover cakes of the Jews and in the 'damper' of the Australian settler. The charging with carbonic gas is commonly effected by fermentation with leaven or yeast; alternative methods involve the use of baking powders (*q.v.*) or the direct injection of the gas. In addition to producing gas, fermentation has a profound effect on the constituents of flour, and improves the flavour and digestibility of the loaf.

The mechanical result of aëration is the creation of innumerable vesicles or cells within the dough, which are subsequently distended by heat, the whole mass being encased in the baking within the crust of dextrin formed by the action of heat upon the starch. The making of bread from wheaten flour is only possible because the latter contains gluten. Gluten is a mixture of proteins which becomes viscid when mixed with water, and, when blown up with gas, has sufficient coherence to remain in the form of a honeycomb instead of collapsing and allowing the gas to escape.

Leavening (Lat. *levo*, to rise) has been practised from time immemorial in the East; from the Egyptians it passed to the Greeks and thence to the Romans, whose conquests and colonies extended the art. It consisted in the first instance probably in a natural fermentation of the dough by leaving it to become sour; but to hasten the process it became usual to add to new dough a portion of old fermented paste or 'leaven.' More recently, yeasts were substituted for the piece of leaven. These were of various origin, that from the distillery being the most suitable. To-day, 'pressed' or German yeast, which consists of yeast grown in a special way, purified by repeated washing and compressed into cakes, is the most generally used. This keeps well, is uniform in quality, and enables the baker to exercise a close control over the regularity of the process.

Dough consists roughly by weight of two-thirds flour and one-third water, the quality of the water being a matter of some importance. The softer the water the quicker is the fermentation, and since the quality of the bread depends on fermentation being allowed to proceed to exactly the right point, it cannot be carried out under precisely the same conditions with hard as with soft water.

Chemistry of bread making.—The chief constituents of flour, so far as bread making is concerned, are (1) the carbohydrates, (2) the proteins. The former include sugars and starch, the proteins consist of a small proportion of soluble protein and a large proportion of insoluble gluten.

The gas formed during panary fermentation is produced by the action of the yeast organism on dextrose. Flour contains about 1 p.c. of sucrose and a little raffinose: before fermentation, both these sugars are converted into dextrose by the enzyme *invertase* present in yeast. This amount of sugar would not suffice to give the necessary amount of gas, but it is supplemented by the maltose produced from the starch of the flour, maltose being itself converted into fermentable dextrose by another enzyme *maltase* contained in yeast.

The formation of maltose is effected by the agency of a diastatic enzyme present in flour; it begins directly the flour is wetted and continues throughout fermentation until the loaf is baked. Yeast contains no diastatic enzyme, but it is possible that its action on the proteins of flour facilitates the production of diastase.

Gas escapes from the dough throughout the process of making a loaf, and the supply available must be sufficient to distend the loaf and maintain it fully distended until it is fixed in the oven. Flours which have relatively little diastatic enzyme will produce insufficient gas, and this fact explains perhaps the beneficial results sometimes obtained on adding malt extract, which is rich in diastase, to dough. This question is in reality somewhat more complicated in that diastase consists of two enzymes—a liquefying enzyme which renders the starch soluble, and a hydrolysing enzyme which converts it into maltose. It is the former rather than the latter enzyme which is sometimes lacking in flour.

Gluten is the characteristic and the most important constituent of flour (v. GLUTEN). It is the agent which principally determines how much water a dough will take; what length of time it requires to be fermented; what will be the size of the loaves, and their colour, flavour, and general appearance. The baker requires quality rather than quantity: the relation between chemical constitution and quality is not yet fully understood (*see* British Association Report on Wheat, Winnipeg, 1909). During fermentation, gluten becomes softer and at first more elastic, subsequently it softens still further, loses elasticity, and begins to break down. Baker's yeast always contains lactic acid organisms, and the conditions in a long sponge are favourable for the formation of this acid, which has a marked solvent and disintegrating action on gluten. Accordingly, in a long sponge, the gluten is considerably disintegrated. The baker's art consists in taking the sponge when sufficiently mellow. If under-fermented, a foxy crust is obtained; if over-ripe, the gluten becomes too much disintegrated and the loaf is less bulky, inclined to crumble, and in extreme cases becomes sour.

Common salt is very generally added to bread. This is done firstly to give the necessary flavour, as owing largely to the action of salt in stimulating the palate, minute quantities of other substances can be recognised in its presence. Secondly, salt has a toughening and binding effect on gluten, though it has a solvent effect on some of the proteins of flour. In view of the modern theory that the properties of gluten are due to small quantities of associated salts, the effect of the added sodium chloride must be taken also into account. Salt also checks diastatic action and fermentation to some extent. Use is made of this property by the baker in dealing with sponges which are over-ripe: a little more salt than usual is used in making the dough, and the subsequent fermentation is retarded and the disintegrated gluten somewhat toughened.

To make a large, well-aërated, shapely loaf of good colour and flavour, it is necessary to use a large proportion of flour from strong wheats. Such a flour usually contains more nitrogenous compounds than a weak flour. Commercially, a demand has arisen for strong flours, which accordingly realise a higher price than weak flours. The strongest flours come from parts of the United States and Western Canada, also from Hungary. English wheats give, as a rule, weak flours, which by themselves are unsuited for modern bread making.

It is the object of the large millers to produce a brand of flour suited for bread making which is a blend of several wheats, and to maintain this brand of flour of uniform quality throughout the year. The preparation of sample loaves, made under carefully standardised scientific conditions, still remains the most satisfactory test of quality, and many flour mills maintain a laboratory for this purpose.

According to Humphries, the starch of flours made from wheat grown in hot, dry climates is very stable and resists disintegration. Such flours require special treatment, the addition of malt extract being a very common process. This addition generally causes an improvement in flavour, due, it is supposed, to the production of dextrinous products, which further have the effect of making the bread more moist.

There is a loss of weight during panary fermentation, due to the conversion of carbohydrates into alcohol and carbon dioxide. Jago estimates this loss at 1·3 p.c.; other authorities give somewhat higher values. Experiments made at Pittsburg indicate that over two-thirds of the total fat present in flour is lost during baking.

The manufacture of bread. To-day, in large towns, bread is usually made in bakeries on a manufacturing scale, and machinery is employed for the mixing of the dough, weighing and moulding of the loaves, whilst the baking is carried out in large draw-plate ovens.

There are various systems of bread making depending on whether the dough is made right off in one operation, or whether a portion of the flour, the yeast and the water, are first made up into a loose paste—the sponge—and the rest of the flour added some hours later. A third system involves the preparation of a ferment most commonly consisting of potatoes, boiled and mashed with water to which a little raw flour is added. The yeast is introduced into this and fermentation carried out so as to favour growth and reproduction and get the yeast in a particularly active state. Flour is added to make a sponge, and this, some hours later, made into dough. The longest system of fermentation is that practised in Scotland. An eighth or tenth of the flour is made into a fairly tight dough with a little yeast and allowed to lie 14 to 18 hours, during which time the gluten becomes almost entirely soluble, and the dough acquires a distinctly vinous smell and taste. It is then broken up with flour and the remainder of the liquor to a thin sponge, which lies about 1½ hours till it shows signs of turning and is then made up into a rather soft dough. The long systems formerly in use, were partly the result of custom and partly due to the slow working yeasts used. To-day, particularly in large bakeries, the tendency is in the direction of the straight dough, though the sponge-and-dough method is very largely practised. It has been claimed that the longer processes require less yeast, make bulkier bread, and bread of better flavour.

When the dough is ready it is scaled off and kneaded into shape. This presses out nearly all the gas and toughens the gluten; if it is not thoroughly done the loaf is likely to contain holes. The loaves are next put aside in a warm place to prove, during which the gluten relaxes and the yeast expands the dough evenly. Too much proof must be avoided, as on putting the bread in the oven the excessive expansion is frequently followed by the collapse and flattening of the loaves. The loaves are then baked at 450°-500°F., a 2-lb. loaf requiring about 40–50 minutes. During baking, the gases are at first expanded and the dough swells, the yeast is killed, some of the starch cells burst, the heat sets the gluten and the starch, and finally the crust is converted into dextrin and in part caramelised.

It is the baker's object to get the maximum number of loaves from a sack of flour. Accordingly, that flour is selected which has the greatest power to take up and retain moisture. Such flours are often termed strong. A sack (280 lbs.) of good flour yields about 96 quartern loaves.

Vienna bread is a term applied to rolls and light fancy bread baked in an atmosphere entirely charged with steam, to obtain which a special oven construction is adopted. The starch of the flour is burst by heat and changed into dextrin by the aid of moisture, so that a rich golden-brown highly glazed crust is obtained.

Leavened bread.—In France and elsewhere on the Continent, bread is made from leaven, but in the more important towns this mode of bread making has been given up for the Viennese and English processes. The practice in the preparation of the leaven consisted in a series of stages ('levain de chef, levain de première, levain de seconde, levain de tout point'), by which, starting with a piece of dough put away from a previous baking and adding at intervals more and more flour and water, the required quantity is leavened. From this is taken a half, which when baked yields a dark, sour bread; the remainder, being again mixed with a quantity of flour and some yeast, produces a whiter and less sour dough, a portion of which is baked and the residue once more added to fresh flour. This subdivision is repeated three times, the bread improving at each stage. A characteristic example of leavened bread is seen in the rye bread (Schwarzbrod) of Germany.

Next to wheat, rye is the chief bread-making grain throughout the world, and in particular it is largely used in Northern Europe. Rye bread is moister, closer, and darker in colour than ordinary household bread. There are several qualities, differing in the proportion of bran contained, the so-called 'pumpernickel' being an extreme example. Fine rye bread is as digestible as wheaten bread, but in the case of pumpernickel a very large proportion is unabsorbed (Romberg, Archiv. f. Hygiene, 1897, 28, 244).

Baking Powders.—Carbon dioxide may also be generated within dough by the action of baking powders, which are usually mixtures of sodium carbonate and some acid or acid salt, and evolve gas when moistened or heated. Owing possibly to the difficulties of distributing fresh yeast, baking powders were formerly widely employed in America. They are not used much in this country for white bread. They are usually classified according to the acid constituent, as tartrate, phosphate, or alum powders (v. BAKING POWDERS). The so-called self-raising flour contains baking powder already mixed with it.

Aërated bread is made by injecting carbon dioxide into dough by mechanical means. The process was originated by Dr. Dauglish in 1859, and at one time enjoyed considerable popularity, but it has not met with universal favour on account of the raw and insipid taste of the bread, due to the absence of the products which yeast produces during fermentation. The carbon dioxide is produced separately and forced into water under pressure: this water is mixed with the flour in a specially constructed vessel, in which the pressure is maintained. On opening the vessel, the dough rises and can be immediately baked. The advantages claimed for the system are uniformity of result, and the avoidance of the losses in weight which occur during fermentation. A later development consisted in mixing a little wort, made from malt and flour and fermented till sour, with the water to be aërated, so as to improve the flavour. The process is eminently suited for the manufacture of whole-meal bread, as the preparation of a batch of dough can be effected in thirty minutes.

Composition of Bread.—The general composition of bread is very variable. About two-thirds of the volume is made up of gas. By weight it contains 40–50 p.c. of water and 6·5 p.c. of protein, the balance being mainly carbohydrate. Hutchison gives the following mean figures for a number of breads analysed by him:—

	Water	Protein	Fat	Carbohydrates	Cellulose	Ash
White . .	40	6·5	1·0	51·2	0·3	1·0
Whole meal .	45	6·3	1·2	44·8	1·5	1·2

On keeping, a loaf gradually loses moisture to the extent of 8 p.c. in 48 hours, 14 p.c. in 72 hours (Goodfellow) or 14 p.c. in 1 week (v. Bibra). At the same time, the bread becomes stale, but this change is not attributed to loss of moisture, as much of the freshness is restored on heating, during which considerably more water is lost. It is suggested that staleness is due to a gradual combination of water with the starch or gluten which is readily broken up by heat; or, alternatively, that it is due to the shrinkage of the fibres which form the walls of its visible pores.

Katz (Zeitsch. physiol. Chem. 1915) has shown that, whereas the softening of the bread crust is due to the absorption of moisture, the crumb will become stale even when no loss of moisture takes place.

The experiments indicate that when bread crumb is kept at ordinary temperatures and loss of moisture prevented, the starch becomes harder and the amount of water-soluble polysaccharides diminishes, the latter being suggested as the cause of the sweeter taste of new bread as compared with stale.

The gluten appears to absorb moisture from the starch granules as staling proceeds, the latter shrinking, with the result that the granules are readily separable from the gluten, thus causing the bread to become crumbly.

The shrinkage of the granules can be seen with the microscope, narrow air spaces being observed between the granules and the gluten.

The adulteration of bread with alum, zinc, and copper sulphates, lime, &c., is now entirely a thing of the past. These were added to prevent the injurious effects of an excess of diastase on the starch during panary fermentation when inferior flour was employed. The cheapening of flour and the critical demands of the public for a well-risen white loaf, as well as improvements in the miller's technique, have necessitated the use of the best flours in bread.

The question of colour, meaning brightness of appearance in crumb and crust, is an important one; at the moment, the demand is for a white loaf. Colour is largely a question of optics; a weak but very white flour may make poor dingy-looking loaves, whilst a darker, stronger flour will make loaves which are better aerated and hence appear much whiter.

A modern development is the artificial bleaching of flour, usually with nitrous fumes produced by some electrical process. There is no proof that bread made with bleached flour is deleterious to health, but its use has been forbidden in America under the Pure Food Laws. It is a matter of controversy whether bleaching by nitrogen peroxide is due to oxidation or to nitration. Bleaching does not change a low-grade flour into a higher one, and bleached flour should therefore be declared as such.

The souring of bread is one of the baker's problems. It is the result of a combination of bacterial fermentations, the bacteria being introduced by the yeast, by the flour, or, as should not occur, by the use of dirty vessels. The flavour of fermented bread improves gradually as the process proceeds until a maximum is reached, after which, if fermentation is continued, it begins to deteriorate. At this stage the alcoholic ferment is exhausted and the acid fermentation begins to predominate. The sourness is mainly due to lactic and acetic acids, the odour to acetic and sometimes butyric acids (J. Soc. Chem. Ind. 1916). A cause of mustiness in bread has been traced to the presence of *Rhizopus nigricans* and *Aspergillus* in the flour from which the bread was made.

Extracts made from such flours when mixed with good flour caused mustiness or sourness in the resulting bread.

Such bread-diseases as ropiness (*cf.* E. J. Watkins, Ropiness in Flour and Bread, J. Soc. Chem. Ind. 1906, 350) are due to specific bacteria. According to Kayser and Delaval, ropiness is due to bacteria of the genus *Mesentericus*, originating in flour. The spores form rods 3–6 μ long and 0·4–0·6 μ thick, sometimes united in pairs and very resistant to chemical and physical reagents. The development on bread is very rapid with abundant spore formation. The bread becomes yellowish-brown, soft, and viscous and acquires an objectionable smell. The addition of lactic acid to the dough with from 30 to 45 minutes baking, depending on the weight of the loaf, prevents the germination of spores.

In a modern bakehouse, bacterial diseases should not occur; they may often be traced to the use of unsound flour.

Whole-meal Breads.—The majority of the patent breads belong to the 'brown' variety, and contain more of the wheat grain than the white flour. In some, the finely ground bran is introduced, in others the germ, whilst a third class claim to contain the complete wheat grain. Bran is very rich in diastatic enzyme, here termed cerealin, and its introduction causes a very rapid conversion of the starch into dextrin and sugar. This causes the dough to become soft and clammy and to bake brown: in addition, it becomes very prone to souring. The use of sodium bicarbonate and hydrochloric acid for aërating whole-meal bread is common. When the fermentation process is used, the bran is not introduced until the dough stage. Whole-meal bread has a great tendency to become sodden; it has to be baked for a considerable time, and consequently often has a thick crust. Germ has a very injurious effect on flour, owing to its diastatic character, and the tendency to become rancid. Every effort is therefore made to remove it as completely as possible. When subjected to the action of superheated steam, the germ is cooked, the diastatic properties are destroyed, and it acquires a pleasant malt-like, nutty flavour and aroma. This process was patented by R. Smith of Macclesfield, and a mixture of one part of treated germ and three parts of white flour constitutes Hovis flour, from which Hovis bread is made.

The relative nutritive values of white and whole-meal bread is a highly controversial subject. It is claimed that whole-meal bread is richer in protein and so more valuable, but this is far from being generally true. A second contention is the larger amount of mineral matter, especially phosphoric acid, in the brown bread. This is certainly true, but experience has shown that the mineral matter is not all absorbed from white bread, whilst in whole-meal bread the quantity absorbed is so much less that it is probable the blood obtains much the same amount from both (Hutchison). Whole-meal bread is defectively absorbed, owing to the cellulose which it contains preventing the gastric juices from gaining access to the neighbouring nutritive ingredients, and for the same reason it interferes somewhat with the absorption of other foods. When the unsatisfactory nature of the whole-meal bread itself and the precautions necessary in its manufacture are taken into consideration, its universal use in times of plenty is not to be advocated. With bread containing added germ the case is different, the bran is absent and the food value, both as regards protein and phosphate, is larger than of white bread.

The use of flour containing the untreated original germ of the wheat berry for bread is, none the less, disadvantageous, since the flour easily becomes rancid and the germ enzymes commence to act on the gluten from the moment the flour is made, causing the loaf to be of poor colour and to be less finely vesiculated and digestible. These factors more than outweigh the advantages of the very small additional amounts of protein, oil, and phosphate introduced and the slightly sweeter flavour of germ bread. The germ contains 10–12 p.c. of oil, which, it is stated, can be used for the production of margarine. Under war conditions in Germany arrangements were made to collect the germ from the mills and extract this oil. The residue of the germ yields a valuable protein food. The germ also contains such vitamines as are present in the wheat-grain. If the vitamines which are considered as essential to the maintenance of health, are to be obtained from none of the other foods eaten in the dietary, then wholemeal bread will have obvious advantages over that made from white flour. However, in actual practice this is not the case.

The desire for more phosphates can be met by the addition of phosphoric acid to the flour, as is indeed being done at the present moment during the milling process in order to improve the quality of flour (*cf.* Humphries, Eng. Pat. 13135 and 17279 of 1908; Chitty and Jago, Eng. Pat. 22434 of 1909; Levin, Eng. Pat. 3073 of 1910).

Under the stress of war conditions both milling and baking practices were altered, and every effort was made to render the maximum possible proportion of the wheat grain available for human food. Millers were only allowed to manufacture straight run flour, and the percentage to be extracted from wheats of various origin was laid down in numerous orders under the Defence of the Realm Act. This amounted to 81 p.c. for English and hard Manitoba wheats, and 83 p.c. for Indian and Australian varieties. In addition, not more than 25 p.c. and not less than 10 p.c. flour from other cereals was to be mixed with the wheaten flour. Bread was to be at least 12 hours old before it was sold.

Authorities.—Jago, Science and Art of Breadmaking, London, 1911; Hutchinson, Food and the Principles of Dietetics, London, 1911; *Wheat*: Brit. Ass. Report, Winnipeg, 1909; Hamill, Local Govt. Board, No. 114, 1911.

E. F. A.

BREAD FRUIT. The fruit of *Artocarpus incisa* (Linn.). The tree grows freely in tropical islands, and yields fruit continuously for 9 months in the year. The fruit is nearly spherical, and sometimes weighs 5 or 6 lbs. It is usually gathered while yet unripe, *i.e.* before its starch has changed into sugar; sometimes the unripe fruit is peeled, wrapped in leaves and cooked whole, when a product resembling ordinary bread is obtained; or the unripe fruit is dried, powdered, and sifted, yielding a flour which has the following composition:—

Water	Protein	Fat	Starch	Fibre	Ash
14·3	1·0	0·2	83·8	0·2	0·4

(Balland, J. Pharm. Chim. 1903, 17, [10] 476).

The leaves and wood of *Artocarpus incisa* are devoid of colouring matter (A. G. Perkin, Chem. Soc. Trans. 1898, 73, 1019). A closely related tree (*Artocarpus integrifolia*) bears a still larger fruit, 'jak fruit,' weighing about 25 lbs., of which about 26 p.c. is flesh, the remainder being rind 66 p.c., and seed 8 p.c. The flesh, when ripe, contains about 5 p.c. of sugar, mainly cane sugar (Prinsen, Geerligs, Chem. Zeit. 1897, 21, [72] 719).

H. I.

BREAN *v.* Oleo-resins.

BREEZES. (*Braise*, Fr.) The dust of coke or charcoal. The coke burner applies this term to the small residual coke obtained in coke burning. The sifted ashes removed from houses is called 'breeze,' and sold under that name to brickmakers and others. An arrangement for burning breeze is described in J. Soc. Chem. Ind. 5, 425.

BREÏDIN, BREÏN *v.* Oleo-resins.

BREMEN BLUE and **BREMEN GREEN.** Pigments containing a basic copper carbonate with alumina and calcium carbonate.

BREWING. Beer is made from water, malt, and hops. Raw, prepared grain, or sugar is often substituted for a portion of the malt, and some other vegetable bitters occasionally for a portion of the hops.

Water used in brewing must be free from sewage pollution, poisonous metals, or substances which may affect the flavour of the beer, such as iron.

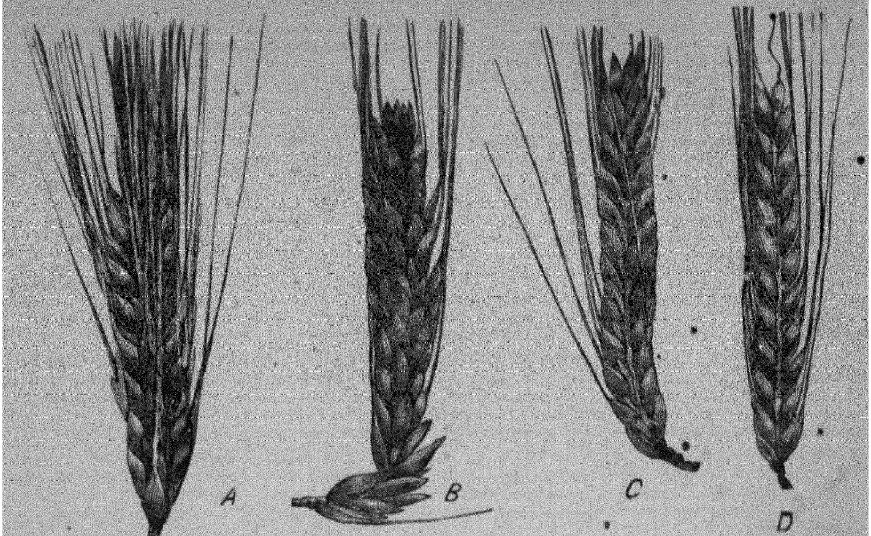
The composition of the water used in mashing has an important effect on the final product. Indeed, it may be considered that the reputation of the best-known brewing districts was initially due to their natural water supplies. The following table gives the amounts of the more important constituents of some of these waters. The figures represent parts per 100,000:—

	Burton	Dublin	London	Munich	Pilsen
CaO .	20–40	14	2–10	10–20	4–10
MgO .	5–15	1	1–2	3–4	2–4
SO_3 .	40–80	1–4	1–20	2–4	2–14
CO_2 .	15	10	4–35	10	3–5
Cl . .	4	2	2–10	6	1–4
Na_2O and K_2O .	6	1	4–20	—	2
Nitrates .	2–10	—	—	—	—

The Burton waters, by means of which are produced the finest pale and strong ales, are characterised by calcium sulphate with smaller quantities of carbonate, and magnesium sulphate and carbonate. Small quantities of chlorides and nitrates are usually present, even in waters which are free from sewage pollution. The amount of calcium sulphate varies considerably in the different wells, owing to the uneven distribution of the gypsum in the formations through which the water percolates.

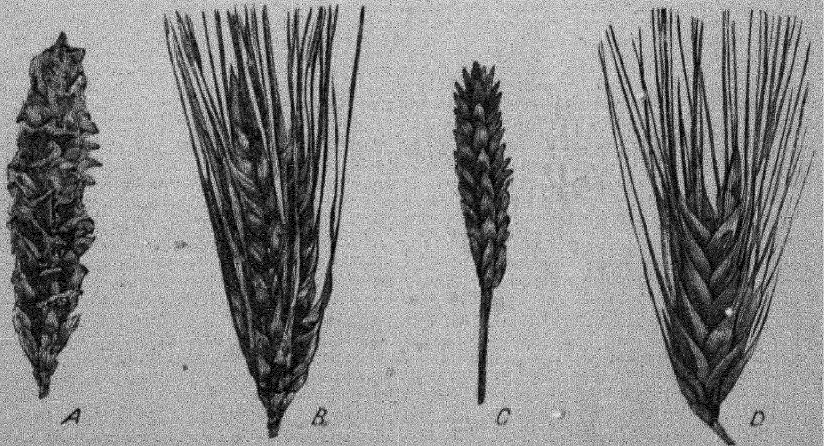
The Dublin water used in brewing the well-known stout has its chief constituent, calcium carbonate, removed by boiling before use, so that as used in the mash tun it is a very pure water.

The London waters are used for beer and stout brewing, but although the beers are not much known outside the district, London porter has more than a local reputation. They are chiefly characterised by calcium and sodium carbonate; sulphates and chlorides are also usually present. Some show a high amount of sodium chloride, and are, no doubt, contaminated by sea water, and if more than 100 parts NaCl per 100,000 are present are unsuitable for brewing.



TYPICAL SPIKES OF THE FOUR SPECIES OF CULTIVATED BARLEY.

A, Hordeum vulgare; B, Hordeum intermedium; C, Hordeum distichum; D, Hordeum deficiens.



SPIKES OF FOUR FORMS OF BARLEY, SHOWING SEVERAL COMMON CHARACTERS.

A is hooded; B and D are awned; C is awnless; A and B are naked; C and D are hulled; A, B, and C have narrow outer glumes, and D wide outer glumes.

FIG. 1.—VARIETIES OF BARLEY.

The Munich waters are very similar to the Dublin waters, and the dark full-flavoured lager is their product.

The Pilsen waters are extremely pure, and in the small amount of salts the carbonates do not dominate the sulphates, as in the Dublin, London, and Munich waters. The lager beer produced is a pale and delicate beer.

Waters containing sodium chloride up to 50 parts per 100,000 are considered suitable for brewing mild ales.

Where the natural water does not conform to one of these types, it is usual to make some attempt at imitating it by the addition of one or more salts. Thus, if pale ale is to be brewed, calcium sulphate or chloride is added; if mild ale, a smaller proportion of calcium salts and a little sodium chloride. For brewing stouts, the water is softened by the addition of suitable salts. In general, calcium and magnesium carbonates are removed by boiling or by heating under pressure with agitation. Such treatment, although resulting in a better beer, is said not to equal that obtained by the untreated natural waters.

Much has been written in order to explain the effect of the dissolved salts. Waters containing calcium sulphate produce pale, delicate beers which clarify well; calcium chloride appears to have similar effects. Calcium salts remove much phosphoric acid. Malt always contains more of this than the yeast requires, and it is possible that a removal of a portion may be beneficial, although it is conceivable that under some conditions, such as the use of a large proportion of some malt substitutes, too much might be removed. Magnesium salts do not give such satisfactory results; the beers have a reddish shade, and do not clarify so well. Sodium chloride produces a sweet flavoured beer. Calcium and magnesium carbonates give dark, harsh flavoured beers, which do not clarify easily, and these effects are accentuated if sodium carbonate is present.

On the whole, the evidence indicates that although the nature of the dissolved salts has some effect, yet the chief results are due to the change which the salts produce on the hydrogen ion concentration when the malt is mashed with the water.

The effect of acidity on enzyme action is well known, and the bad effects of alkaline waters are largely due to their restrictive effect on enzyme action. Schjerning (C. R. de. trav. du Lab. de Carlsberg, 1913, 312) measured the hydrogen ion concentration of worts made with waters containing various salts. He found calcium sulphate and chloride and magnesium sulphate and chloride, when about 100 parts per 100,000 are present, all raised this from P^h 6·1 to 5·7. That sodium chloride and sodium sulphate had no effect, and that calcium and magnesium carbonates lowered it. He also found that P^h 5·5 was the most favourable for enzyme action on the carbohydrates, and 5·3 for the proteid transformation, and that slight changes between this and 6·1, the normal P^h of malt worts prepared with distilled water, have a marked effect on these actions. Sherman and Thomas (J. Amer. Chem. Soc. 1915, 625) find a P^h 4·2 to 4·6 for the maximum diastatic action. The effects of these salts on enzyme action have been confirmed by other authors. H. T. Brown (J. Inst. Brewing, 1909, 216) and Weiss (C. R. du Lab. de Carlsberg, 1903, 216) found that calcium salts increased the amount of soluble nitrogen compounds, and many others have observed the effect on starch transformation.

Malt contains primary and secondary phosphates, and it is easy to construct an equation showing how calcium salts may increase the acidity, thus :—

$$4K_2HPO_4+3CaSO_4 =2KH_2PO_4+3K_2SO_4+Ca_3(PO_4)_2$$

Other equations may be written, showing the formation of dicalcium phosphate, but as this is also insoluble, the result will not be affected. It may be otherwise with magnesium salts, as dimagnesium phosphate is soluble, and this may explain the less satisfactory effect of magnesium salts. On the other hand, Schjerning found them to have the same effect on the hydrogen ion concentration as calcium salts.

The preference of brewers for hard water for brewing beers thus seems explicable; but the equally well-established fact that soft water must be used for stout does not appear so evident. The lager beer brewers also find hard waters unsuitable. Some Continental authorities have gone the length of stating that the most suitable brewing water for all purposes is water free from dissolved salts, but the faith of the pale ale brewer in his sulphated water remains. *See* also O. Miskowsky, Zeit. f. d. ges. Brau. 1911, 49 and 97; Windisch and Goldacker (Jahresber des. Ver. u. Lehranstalt f. Brauerei, Berlin, 1916; Readman, J. Soc. Chem. Ind. 1894, 367; Lott, Trans. I. Br. 1897, 344; Matthews, Trans. I. Br. 1893, 109, and 175).

Malt is made from barley, occasionally from wheat or oats. Barley used for malting is mainly of four different varieties:— Fig. 1.

A. *Hordeum vulgare* (*hexastichum*), found in commerce as Chilean barley, sometimes Syrian.

B. *Hordeum intermedium*, found in commerce as North African and Smyrna barley. Bere.

C. *Hordeum distichon*, found in commerce as Goldthorpe, Chevalier, &c.

D. *Hordeum deficiens*, Bulletin 622, Bureau of Plant Industry, Washington, U.S.A.

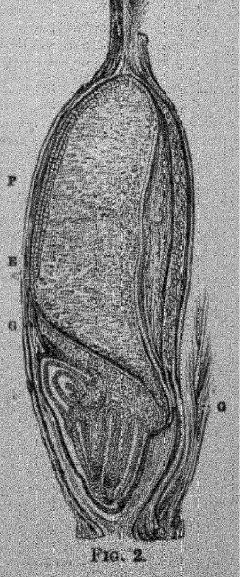


FIG. 2.

The barley corn consists of three chief parts, the coverings (the paleæ (P), the endosperm (E), and the embryo (G) (Fig. 2).

The coverings contain the greater portion f the cellulose and cellular matter, and a larger roportion of ash than the remainder of the orn; the endosperm contains the starch and ome reserve proteid.

The six-rowed barleys, the first two on the bove list, are smaller than the two-rowed arleys, roughly in the proportion of 3 : 4; he proportion of endosperm to the remainder f the corn is smaller, and consequently they ontain less starch. The chevalier barleys conain a less weight of skin (paleæ) than the oldthorpe.

The following table summarises the most rustworthy data obtained from the analyses f barley. Whilst the relative amounts of the onstituents differ, the same substances are resent in all ripe barleys used in malting, hether of different varieties, or grown under ifferent climatic conditions. Barley may be onsidered as normally containing 14 p.c. of oisture.

Average Composition of Dry Barley.

Starch	50–60 p.c.
Gums	9–10 ,,
Nitrogen compounds .	8–14 ,,
Sugar	2 ,,
Fat	2–3 ,,
Cellulose and fibre . .	15–30 ,,
Ash	2½–3½ ,,

The gums are hydrolysable to glucose, rabinose, and xylose (Lindet, Compt. rend 903, 73; O'Sullivan, Chem. Soc. Trans. 1882, ; Brown, Trans. Guiness Lab. 1906, 312).

Nitrogen compounds. 45 p.c. are insoluble n water and alcohol; 35 p.c. insoluble in water, ut soluble in 75 p.c. alcohol (hordeine); and 0 p.c. soluble in water (leucosin, edestin, &c.) Osborne, Amer. Chem. Soc. 1895, 539).

Sugars consist chiefly of cane sugar with a ittle raffinose and glucose (O'Sullivan, Chem. oc. Trans. 1886, 58).

Fat contains 78 p.c. neutral fat, 14 p.c. ree fatty acids, 4 p.c. lecithin, and 6 p.c. cholesterol (Stellwaag, Zeits. f. d. ges. Brau, 1886, 75).

Cellulose and fibre. About one-third is true ellulose.

Ash consists chiefly of silica and potassium hosphate; probably in the barley the phoshorus is not present as phosphate (Windisch, . C. 1906, 1573). A lipoid or diamino phosphaide has been identified. Barley also contains nzymes, including a diastase of translocation hich does not act on starch paste, but saccharises soluble starch (Kjeldahl, C. R. Lab. Carlserg, 1879, 129; Ford and Guthrie, J. Inst. rewing, 1908, 61).

Malting consists in the partial germination f the grain, by first steeping it in water, then llowing it to grow to a definite amount, and hen stopping the process by drying by heat.

The object in malting is to so modify the ell walls of the endosperm, and produce enzymes hat in the mash tun the starch may be readily issolved; to do this with the least loss by espiration or rootlet; without transforming oo much of the insoluble proteids into soluble ompounds; and avoiding the production of ndesirable decomposition compounds by moulds r bacteria.

It is evident that the first essential is a suitable barley. Such a barley must be mature in the widest sense of the word. If it is, then all the grains will, under the proper conditions, germinate evenly. It must be uniform in size and in composition, both chemically and morphologically. It must be free from damaged corns or foreign grain. Other things being equal, barleys with a high nitrogen content are not so satisfactory.

Elaborate schemes have been drawn up in Germany for the valuation of barley, based on a system of marking of points, but they are too cumbersome for ordinary practice. Experience enables a fair judgment to be made of the malting value of a sample. Unless a barley has been harvested under the best climatic conditions, it is found that its uniformity of germination is improved by drying on a kiln, and this is a common practice. Also that storage for a few months after harvesting is for the same reason advisable.

The malting process is commenced by steeping the grain in water. The steeping cistern is usually of brick or iron, and provided with a perforated bottom for drawing off the water.

It is usual to use a moderately hard water, such as would form a good domestic supply, but as some authorities advocate the addition of lime-water, it would appear that a slightly alkaline water is quite suitable.

Two or three days are necessary at a temperature of 10°–13° C. (50°–55° F.); the thicker-skinned varieties taking the longer time. About 50 p.c. of water is absorbed, and the grain becomes quite soft to the finger-nail.

One of the inner coatings of the barley grain is semi-permeable, and will not allow any of the soluble constituents to pass from the interior, nor admit anything but pure water from such waters as are likely to be employed for steeping (A. J. Brown, Proc. Roy. Soc. 1909, 81). A considerable amount of matter is extracted from the surface and outer skin of the grain, and, of course, from the interior of damaged corns. As numerous bacteria, &c., are always adherent to the surface of the barley, the water soon becomes putrid, and it is therefore customary to change the steep water several times.

The drawing off and renewal of the water aërates the steeping barley, and this is found to be beneficial.

Too long a steeping impairs the vitality of the corn, and too short does not allow sufficient water to be absorbed to carry on the germination sufficiently.

It is probable that germination commences during steeping, but the amount of change is small.

After steeping, the grain is thrown out of the cistern on to the growing floors. These are made of cement or tiles. Chitting soon begins, leading to the production of rootlets, and the plumule begins to grow. Owing to the adherence of the paleæ, the plumule grows up the side of the corn under these, and does not emerge until it reaches the distal end of the grain. The rootlets emerge from the proximal end of the grain. These outward appearances of germination are accompanied by profound change in the interior of the grain.

Germination is an enzymic process of demolition, followed by a building up. The embryo sécretes enzymes, which break down into a soluble form the reserve matters of the endosperm, and utilise them for its growth. So at any stage before germination is complete there will be a whole series of compounds present in the grain from complex to simple, and again from simple to complex.

One enzyme, *cytase*, attacks the walls of the starch cells; this action is most important, as on its completeness depends the tenderness of the malt. The walls of the starch cells of various barleys differ materially in their tendency to ready dissolution. Generally those barleys most prized for malting are those in which the cell walls give way most easily. These cell walls must be broken down before the starch is available; the products of their transformation form an important food for the first growth of the young plant. This dissolution not only precedes starch dissolution, but proceeds more rapidly, and this fact renders it possible to attack the greater parts of the cell walls before the starch is to any great extent dissolved. The diagram (Fig. 3) shows the process (Brown and Morris, Chem. Soc. Trans. 1890, 469). A at 3 days, B at 6 days, C at 10 days.

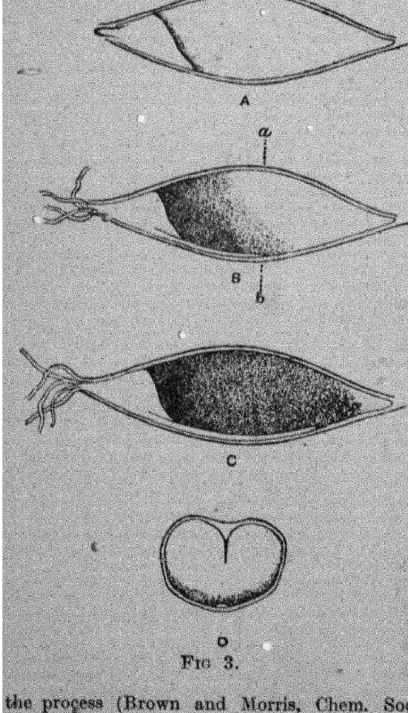


Fig 3.

Amylase attacks the starch and transforms it into sugars, part of which are still found in the finished malt, part utilised by the embryo and part oxidised by respiration to carbon dioxide and water. Proteolytic enzymes attack the reserve protoplasm (Weiss, C. C. 1904, 385); there are probably also fat splitting enzymes, &c.

These changes are affected by temperature, amount of moisture, aëration, and the business of the maltster is to control them. This he does by turning the malt, spreading it in thick or thin layers, sprinkling it with water, and regulating the temperature of the malthouse as best he may. If the temperature be allowed to rise above 12°–13° (55° F.), increased enzyme action leads to larger rootlet production and respiration losses. Increased temperature, accompanied by increased moisture, leads to increase in both proteid and starch degradation products in the finished malt (Brown, J. I. Br. 1909, 190). If too much water be given the plumule (acrospire) grows too fast. Both excess and deficiency of water reduce oxidation and rootlet growth. If the carbon dioxide of respiration is too much dispersed by excessive turning and the grain is too much aired, there is excessive respiration loss. Too little oxygen impairs the necessary germinative changes (Schjerning, C. R. Lab. Carlsberg, 1910, 169; Brown, J. Inst. Brewing, 1907, 394; and 1909, 170). The grain having grown several bushy rootlets, and the acrospire from 2/3 to 3/4 up the grain, it should have arrived at the proper state of endosperm modification; that is, the cell walls should be broken down. 10°–13° (50°–55°F.) is considered the most satisfactory growing temperature (Day, C. J. 1891, 664; Blaber, Brewers J. 1907, 359; Weiss, C. C. 1904, 373). The time on the floor necessary for this is from 10 to 12 days at the usual malting temperature (50°–55°F.), the thin six-rowed varieties take longer. Some Continental malsters floor the malt for a shorter time, but they are satisfied with a less modified malt.

In order to save the considerable amount of labour and space necessary in a floor malting, and to obtain more command over the temperature, several other germination methods have been devised; these go by the general name of pneumatic malting. The steeped barley is placed in rotating drums which are supplied with cooled saturated air, the amount of which may be regulated at will. The difficulty is, that in cooling the malt by a current of air excessive respiration takes place, and this often at the later stage of germination, when a check on respiration is most necessary. A method of overcoming this is to conduct the final stage of germination in the drum or in a box in which the carbon dioxide is allowed to accumulate.

The grain is now ready for the next process that of drying.

The kiln consists of a tall building adjacent to the growing floor. On the ground floor is one or more fire baskets for burning coke or anthracite coal, or a furnace for heating air in case the drying is to be done without bringing the products of combustion in contact with the malt. The former is the British plan, the latter the Continental Above the fire baskets or furnace, is a floor or two floors of perforated tiles or wire mesh, on which the grain to be dried is loaded, and above is a roof with a cowl or other suitable ventilating appliance with adjustable openings. The air inlets on the ground floor are also capable of regulation.

If the kiln has two floors, the drying is begun on the top floor and finished on the bottom floor.

The malt being loaded in the kiln, the temperature is slowly raised so that about 65°–66° (150° F.) is reached in three days, when the temperature is further raised to 93°–94° (200° F.) more or less, dependent on the kind of malt that is being dried.

Owing to the slow rise of temperature, germination continues during the earlier stages of drying; but as the temperature increases the vitality of the corn is destroyed, the enzymes being reduced or altered. The amount of diastase in the dry malt is 1/3 to 1/4 of that in the green malt. In the last period empyreumatic products are produced by the caramelisation of the carbohydrates and proteids, and the well-known biscuity flavour appears. In order to produce this, the temperature and moisture must have a certain correlation. Too much water at a high temperature would produce a cooked product, and too little, not sufficient caramelisation.

If the products of combustion are allowed to come in contact with the malt, care must be taken that the fuel used is free from arsenic. Coal and coke nearly always contain some, so that that variety must be selected which does not contain more than 1/20 grain arsenic per pound.

When the malt is dry, it is removed from the kiln and passed through a machine which first detaches the rootlets by beaters, and then separates them from the malt by screens. When cool, the malt is stored in air-tight bins until required for use in the brewery. If exposed to damp air, it absorbs moisture and deteriorates.

The rootlets or 'culms' form a valuable cattle food, a large part being digestible. Their composition is :—

Fat	1–2	p.c.
Proteids	24–28	„
Carbohydrates	42–48	„
Cellulose and fibre	11–15	„
Ash	6–7	„

100 parts dry Chevalier barley yield on the average 89 parts malt; 4 p.c. is lost in rootlets, and 7 p.c. in respiration (E. S. Beaven, J. Inst. Brewing, 1902, 587).

The changes which take place when barley is converted into malt are complex. In a normally malted barley about 60–70 p.c. of the nitrogen compounds are in some way altered, and about 35–40 p.c. have passed from the endosperm to the embryo. Some of the nitrogenous compounds are removed with the rootlet, so that malt always contains less than the barley from which it is made. On the whole, a large proportion of the insoluble albuminoid of barley is still insoluble in the malt; the hordein is partly converted into a similar body, *bynin*, and partly into soluble nitrogenous compounds of lower molecular weight.

The soluble bodies are further degraded. About 40 p.c. of the nitrogenous bodies are permanently soluble on mashing. The nitrogen in the non-coagulable nitrogenous matters of malt soluble in cold water is distributed as follows: (H. T. Brown, J. Inst. Brewig, 1907, 413):

Ammonic nitrogen	3·5	p.c.
Albumose nitrogen	20	„
Peptone nitrogen	31	„
Amide and amine nitrogen [1]	8·5	„
Organic bases nitrogen (betaine, choline)	4	„
Unaccounted for	33	„
	100	

When mashed, the soluble nitrogen substances will be increased about 50 p.c. Schjerning (C. R. Lab. Carlsberg, 1910, 387) states that 20 p.c. of the total nitrogen of the malt should be tryptic decomposition products (ammonia, amine-amid), and that 5 or 6 p.c. of the total nitrogen amount occurs in the wort as albumin (leucosin). About one-third of the total nitrogen of the malt is soluble on mashing.

From 16 to 18 p.c. of the starch has been transformed into sugars the greatest portion (9–15 p.c.) is found in the malt, a portion has been utilised by the growning embryo, another portion is removed by the rootlet, and some has been lost by respiration.

Malt is always more acid than barley, and it has been suggested that as it usually contains less fat than barley, a portion of this is due to saponification and corresponding liberation of fatty acid. The increased acidity has also been attributed to the work of acid-forming bacteria during the flooring and early stages of the drying.

Malt contains fats containing free fatty acids and unsaponifiable matter; also a lipoid (diaminophosphatide) (Lüers, Zeitsch. ges. Brau. 1915, 97, 125).

Malt, like barley, contains amylans or gums, but we know nothing of the change produced in these by malting.

The cellulose and fibre are very slightly, if at all, affected by the malting process.

There is a little less ash in malt than in barley, as the steep water dissolves about one-tenth of it; the constituents are, however, unaltered.

One of the most important facts for the brewer is the proportion of the malt soluble in the mash tun. This includes all the water-soluble compounds of the malt and those transformed into soluble compounds by enzymes at the mashing temperature. The chief of these is starch, but some of the insoluble nitrogenous substances are also rendered soluble.

The 'extract' varies from 75 p.c. or more for the best two-rowed varieties, such as English, Hungarian, &c., to 70–73 p.c. for Californian and Smyrna, and is as low as 65 p.c. for some of the very thin six-rowed North African varieties.

There is probably more than one amylase, perhaps two; one liquifies, and one saccharifies; but there may be more. It is said that amylase may be extracted by a 50 p.c. aqueous solution of glycerine or a 3 p.c. aqueous solution of pyridene, and that such extracts will retain their activity for years. Maltase is also present (Marino and Fiorentino, Gazz. chim. ital. 1906,

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[1] Chiefly asparagine, a little leucine and tyrosine and a trace of allantoin.

395; Davis and Ling, Chem. Soc. Trans. 1904, 16).

A proteolytic and two peptolytic enzymes are present, the former with an optimum temperature of 56°–58° C., and the latter 25°–37° C., the first is destroyed and the others greatly weakened at 50° C.

Also peroxidase and catalases which exist in barley increase during germination and decrease by kilning (Van Laer, J. Inst. Brewing, 1906, 313; Schjerning, C. R. Lab. Carlsberg, 1910, 200).

Malt, as it leaves the kiln, is free from moisture, but on exposure it quickly absorbs a small percentage. Care must be taken that this does not exceed 3 4 p.c., or the malt becomes slack and deteriorates. Unknown (possibly proteolytic) changes take place which render it unfit for brewing.

As already stated, a portion of the malt is often replaced by substitutes In 1915 British brewers used 76 p.c. malt, 1 p.c. unmalted grain, 6 p.c. maize, rice, and other preparations, 16 p.c. sugars. American brewers used large amounts of raw grain or maize grits. German brewers in pre war days used no malt substitutes, but some used partially malted barley, which more nearly resembled barley than malt. Although no doubt unmalted grain, maize, rice, and their preparations are used on the score of economy, the same cannot be said of the sugar; the use of this is considered to yield a beer that clarifies quicker, but the chief reason is, that a fuller (sweeter) beer is obtained. This is what the public demands.

Maize, rice, and their preparations are used either as grits, consisting of the broken up endosperm free from the germ and coverings, or as the same material flaked, i.e. a form in which the starch has been partly gelatinised by moisture and heat

The sugars in common use are raw cane sugar (not raw beet sugar, which contains nauseous impurities), refined cane sugar, invert sugar prepared by inverting with weak acid raw cane sugar and purifying the product, and glucose prepared by the action of acid on starch (*q.v.*).

Hops give to beer its well-known flavour, and act as a preservative. They also fulfil other important functions in the course of brewing. A characteristic peculiarity of the bitterness of hops is that it is transient, after the beer is swallowed the bitterness at once passes away.

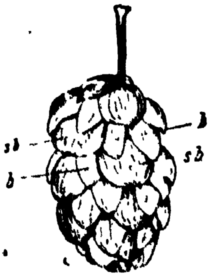


FIG. 4.

(*From Percival's Agricultural Botany, Duckworth & Co.*)

The ripe female flower is the part used in brewing. This consists of a cone of bracts (*b*). At the base of the bracts are the seeds and lupulin glands. Owing to the absence of male plants in the Continental gardens the hops are seedless. English and American hops are seeded owing to the presence of a few male plants in the gardens. There are good reasons for both these practices, dependent on the variety of hops grown. In an experiment made on English hops it was found that seeded hops contained 15 p.c. lupulin compared with 17 p.c. in the same variety seedless, but as the yield was much larger in the first case, 147 lbs. lupulin per acre were obtained in the one case against 92 lbs in the other.

The brewing value of the hop depends mainly on the lupulin The amount varies very greatly, from a few p.c. up to as much as 20 p.c. of the weight of the hop. It contains essential oil, wax, resins, and one or more alkaloids, &c

The essential oil forms 0·2–0·8 p.c. of the hops. It is easily soluble in alcohol and ether, but only in 600 parts of water. Its principle constituents are an aliphatic hydrocarbon *myrcene* $C_{10}H_{16}$, b.p. 166°–168°, and a sesquiterpene *humulene*, b.p. 263–266°, these form 80–90 p.c. of the oil. There are also oenanthylic, caprylic, and pelargonic ethers of myrcenol ($C_{10}H_{17}OH$) (Chapman, Chem. Soc. Trans. 1895, 783; 1903, 505; and Rabak, J. Inst. Brewing, 1915, 75).

Most of the oil is volatilised when hops are boiled with the wort, but as hops are also added to the finished beer, the oil from these latter will remain

The resin is said to consist of two crystallisable slightly acid bitter substances soluble in petroleum spirit, named the α- and β-resins, and a resin (γ-resin) insoluble in petroleum spirit, but soluble in alcohol and not precipitated by lead acetate.

All three are soluble in ethyl-ether and methyl alcohol

The α-acid $C_{20}H_{30}O_5$, m.p. 56° C., precipitable by alcoholic lead acetate, may be oxidised to valeric acid, the β acid not precipitated by this reagent is $C_{25}H_{36}O_4$, m.p. 92°–93° C., on oxidation yields a yellow resin; the γ-acid is stated by some authorities to be tasteless and valueless in brewing, and by others to have a slight bitter flavour and to be capable of coagulating some albuminoids from worts.

Authorities differ as to which of the first two are the more valuable in brewing; the β- acid is usually present in largest amount. Both of these are easily changed by heat or storage into insoluble and presumably less valuable resins The α- and β- or soft resins may be estimated in hops by extraction with petroleum spirit, which also extracts the wax; this may be removed by extracting with methyl ether, in which the wax is insoluble, and weighing the amount extracted; or titrating this with $N/_{20}$KOH, using phenolphthalein and taking 1 c.c. of normal potash as equal to 0·40 gram resin. There is considerable discrepancy concerning these resins in the literature of the subject.

About 2·5 p.c. of tannin is present in hops; whether this is of value as an albuminoid precipitant is uncertain. Hops also contain 0·5–1 p.c. nitrogen compounds soluble in hot water (Chapman, Chem. Soc. Trans. 1914, 1895 and 879). Small quantities of alkaloids are present in hops, and choline has been identified; also carbohydrates, fibre, ash, and moisture. An oil can be extracted from the seeds. Hops contain diastase.

Power, Tutten, and Rogerson (Chem. Soc.

Trans. 1913, 1291) examined the alcoholic extract which was insoluble in water and amounted to 14·1 p.c. of the hops examined. These were New Kent, containing 10·5 p.c. water, 2·4 p.c. tannin, 7·9 p.c. ash. They isolated from it :—

Ceryl alcohol $C_{27}H_{56}O$, hentricontane $C_{31}H_{64}$. A phytosterol $C_{27}H_{46}O$, A phytosterol glucoside $C_{33}H_{56}O_6$. A mixture of volatile fatty acids, consisting of formic, acetic, butyric, valeric, and a hexenoic $C_6H_{10}O_2$, b.p. 204°-208°, and identified as δ-*iso*propylacrylic acid and a little nonoic acid $C_9H_{18}O_2$; saturated and unsaturated non-volatile acids, including palmitic, stearic, and cerotic acids, and an acid $C_{20}H_{40}O_2$, m.p. 62·5°-63°, apparently an isomeride of arachidic acid, cluytonic acid $C_{21}H_{42}O_3$, m.p. 69°; humulol $C_{17}H_{18}O_4$, m.p. 196°, with a bitter taste; and xanthohumol $C_{13}H_{14}O_3$, m.p. 172°, tasteless.

It thus appears that the bitterness of hops is not due to any single substance, but is to be attributed to a number of products, most of which are amorphous. One well-defined bitter substance, *humulol*, has, however, been isolated.

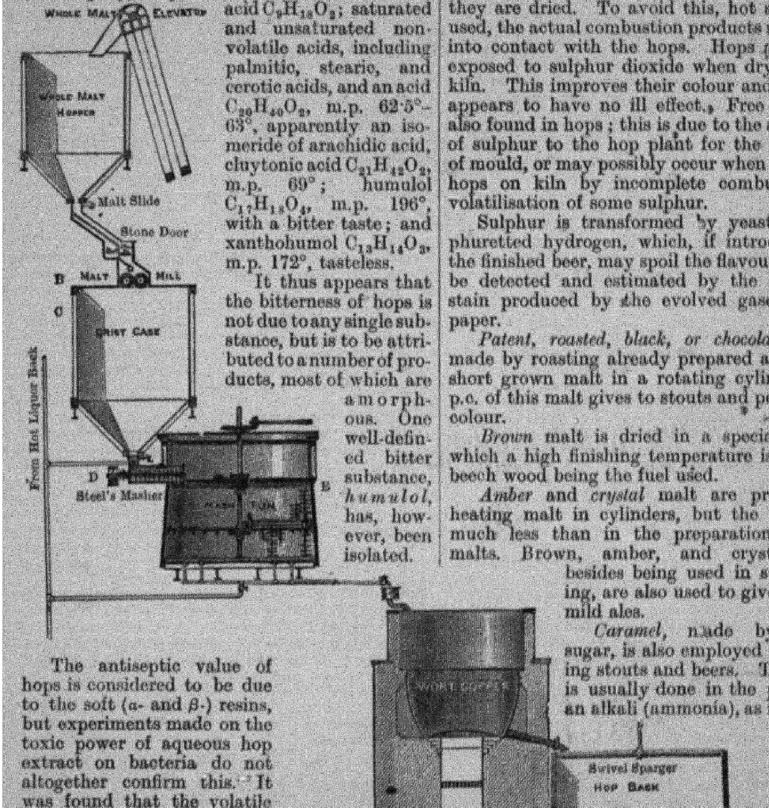


FIG. 5.

The antiseptic value of hops is considered to be due to the soft (α- and β-) resins, but experiments made on the toxic power of aqueous hop extract on bacteria do not altogether confirm this. It was found that the volatile constituents have no antiseptic power, that five-sixths of the antiseptic power was extracted by one hour's boiling with water, but that under these conditions not much of the soft resins was extracted, and the portion extracted seemed to be changed to the hard or insoluble resin. The antiseptic substance was present in true solution, and compared with other antiseptics was weight for weight more toxic to beer bacteria than salicylic acid or potassium metabisulphite (Brown, J. Inst. Brewing, 1910, 641; and 1913, 261).

It thus appears that the nature of the preservative substance of hops is still to be determined, and that the value of the results obtained from estimations of the so-called hard and soft resins is doubtful. In practice empirical methods are employed for valuing hops. These are based on the 'feel' and 'aroma' of the hops when rubbed between the hands. This, in experienced hands, enables a judgment to be made of flavouring and preservative values. It seems likely that the judgment so arrived at on the preservative power is often erroneous; but in the present state of the chemistry of the hop no more trustworthy means is available.

Hops are sometimes contaminated by arsenic derived from the fuel used in the kilns in which they are dried. To avoid this, hot air is often used, the actual combustion products not coming into contact with the hops. Hops are usually exposed to sulphur dioxide when drying in the kiln. This improves their colour and otherwise appears to have no ill effect. Free sulphur is also found in hops; this is due to the application of sulphur to the hop plant for the prevention of mould, or may possibly occur when sulphuring hops on kiln by incomplete combustion and volatilisation of some sulphur.

Sulphur is transformed by yeast into sulphuretted hydrogen, which, if introduced into the finished beer, may spoil the flavour. It may be detected and estimated by the amount of stain produced by the evolved gases on lead paper.

Patent, roasted, black, or chocolate malt is made by roasting already prepared and usually short grown malt in a rotating cylinder. Ten p.c. of this malt gives to stouts and porters their colour.

Brown malt is dried in a special kiln, on which a high finishing temperature is obtained, beech wood being the fuel used.

Amber and *crystal* malt are prepared by heating malt in cylinders, but the roasting is much less than in the preparation of black malts. Brown, amber, and crystal malts, besides being used in stout brewing, are also used to give colour to mild ales.

Caramel, made by heating sugar, is also employed for colouring stouts and beers. The heating is usually done in the presence of an alkali (ammonia), as in this way intenser colours are produced. For chemistry of caramel, *see* Cunningham and Dorée (Chem. Soc. Trans. 1917, 589-608). *V.* CARAMEL.

The first stage of actual BREWING is the grinding of the malt. If the malt were completely modified, that is, if the cell walls of the starch cells were completely disintegrated, this would be a comparatively easy matter, and the simple method of just crushing the grain between two plain iron rollers would be all that is necessary. Although malt never is perfectly modified, yet much that is made is sufficiently so for this method to be employed in many breweries. Still even with the best malts, when crushed by this method, it is possible to detect starch in the residue remaining in the mash tun after extraction is completed. This is due to the fact, as has already been described, that dissolution of the cell wall proceeds from the proximal to the distal end of the grain; and that as even the finest barleys do not germinate absolutely evenly, to avoid excessive loss from overgrown corns, the process must be stopped in many corns before its completion, so that there must be a number of corns containing a smaller or greater 'hard end.'

In order to reduce these 'hard ends' to a condition in which they will dissolve in the mash tun, they must be finely ground. If the whole corn were finely ground, the extraction would be so slow, as to make the process unworkable. Mills have therefore been devised in which the roughly crushed malt is separated by sieves and air currents into various portions, and the grits and hard ends finely ground and re-mixed with the remainder of the crushed malt Fig. 6 is a modern malt mill.

The grinding is usually preceded by treatment in cleaning machinery, in which the malt is brushed, beaten, exposed to a current of air, and sieved. Thus stones, surface dirt, straw, weevily (empty) corns, and other foreign bodies are removed.

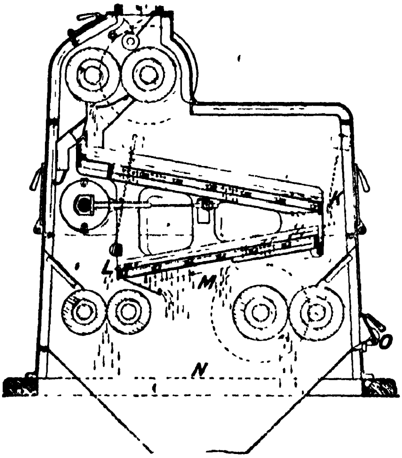


Fig. 6.

The ground malt is collected in receivers (malt hoppers or grist cases) until the amount required for the brew is complete. These receivers command the mash tun, the vessel in which the malt and water are mixed.

Fig. 5 is a diagrammatic representation of the mashing side of a brewery.

Mash tuns (Fig. 7) consist of wood or iron vessels fitted with false bottoms of perforated metal plates. Pipes are connected with the bottom of the tub for drawing off the extract (wort). In the upper portion, or above the tun, are inlets for the malt, hot and cold water; and an underlet for hot water is usually inserted in the bottom of the tun. The tun is generally provided with mixing gear ('rakes'). A sparger for sprinkling hot water on the surface of the mash is required, so that the grains may be thoroughly extracted.

At the proper time, water at a pre-determined temperature and the ground malt are mixed. This is done either by placing in the mash tun sufficient hot water and admitting the malt with constant stirring, or the malt and hot water are admitted together through a special mixing machine, a 'steel' masher being the one in common use (Fig. 8). The mash may now be treated by the 'infusion' or the 'decoction' system.

The infusion system is employed in the production of British beers. The mash (temperature about 65°–66° (150°F.)) is simply allowed to stand for a couple of hours, and the infusion then drawn off, the insoluble residue (brewers grains) is exhausted by sparging with hot water.

The decoction system is employed for the production of 'lager' beers. The malt is usually mixed with water to give a comparatively low temperature mash, 38°–49° (100°–120° F.) (sometimes cold water is used), and allowed to stand at this temperature for a couple of hours; no starch degradation takes place, but it is a favourable temperature for proteid transformations. About one-third of the thick mash from the bottom of the tun is run into a copper (mash-copper) and then boiled for half an hour, after which it is returned to the mash tuns; this raises the temperature of the whole about 30° F. After another interval, a further portion is withdrawn and boiled and returned to the mash tun, and this again repeated if required. The mash is then treated as by the infusion system.

Instead of being extracted in mash tuns, the mash may be pumped into a filter press, and in this way the wort separated from the insoluble residue. Special presses have been designed for the purpose. Larger extracts are obtained, as it is possible to deal with finer ground malt.

When the mixture (mash) is first made, there is a rise of temperature of 2°–3° F. due to hydration or adsorption; the drier the malt, the more heat is evolved. Starch transformation causes a rise of 0·5° F. Important enzymic changes take place in the mash. The chief of these is the saccharification of the starch. There are also important proteolytic changes and other less important enzymatic actions. These changes are influenced by the temperature, fineness of grinding, amount of dilution, duration of the process, and composition of the mashing water, &c. The temperature has a great influence on the character of the starch transformation (*see* Starch). Brewery mashes are usually carried out between 63° and 68° (145° and 155° F.), and about four-fifths of the starch is converted into maltose; 65°–66° (150° F.) is the optimum temperature for quantity.

Proteid transformation is most active at a lower temperature, 45°–55° (113°–131° F.), but the action continues up to about 77° (170° F.). From 5 to 12 p.c. of nitrogen compounds are rendered soluble at 65° (150° F.), and if the decoction low temperature is employed, about 3-4 p.c. additional, but the change is chiefly in the production of more lower-grade bodies.

The fineness of grinding, as has already been pointed out, will affect the amount of extract, but the composition of the wort is not otherwise affected.

The extract increases with the amount of dilution up to 6 water to 1 malt, after which it decreases. This is due to an increase in the quantity of starch saccharified, as the amount of proteid transformation decreases with the dilution. All the enzyme actions reach their maximum amount within the first hour, or, at most, two hours.

The effect of alterations of the mashing water has already been described; the more sparging water is used for extracting, the greater is the amount of nitrogen compound extracted. For this reason brewers do not press the extraction too far.

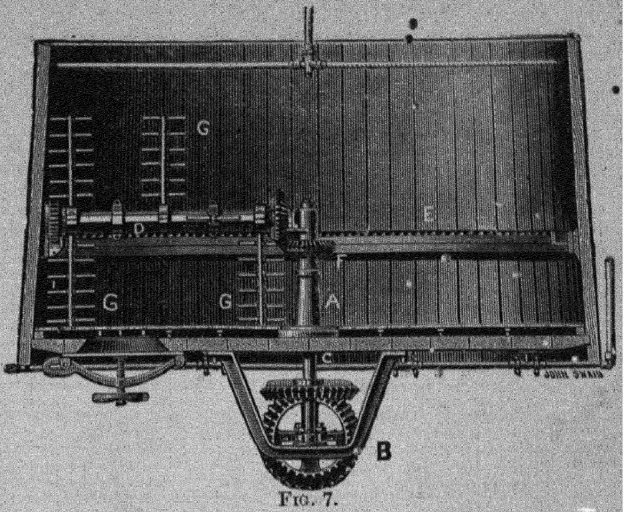


FIG. 7.

When raw grain or grits are used as substitute for a portion of the malt, the starch of these must be first gelatinised by boiling, and this when mixed with the mash is saccharified by malt diastase. It is stated, however, that if the material is finely ground, the starch can be saccharified in the mash tun by the malt diastase without previous boiling. Flaked grits will saccharify in the mash without previous boiling.

Sugars are usually added to the wort in the copper.

The draff or 'grains' remaining in the mash tun after extraction is completed, forms a valuable cattle food. It may be used fresh, and then contains about 70 p.c. water; in this state it does not keep well. If dried, it keeps indefinitely.

The composition of the dried product is :—

Carbohydrate .	41
Proteid . . .	22
Fat	7
Fibre . . .	16
Ash	4
Water . . .	10
	100

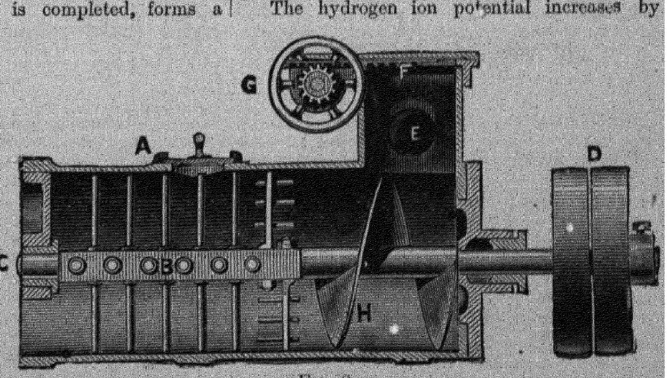


FIG. 8.

The mash tun wort as it flows from the mash tun is collected in a wort receiver or underback, and thence is conducted into the coppers where it is boiled with hops.

These vessels, as their name indicates, are made of copper (although iron vessels are also said to be used for this purpose) and heated by fire or steam. The amount of hops used varies with the quality of the beer to be brewed. Ordinary mild ales require about 1 lb. per barrel, bitter beers from two to three times this quantity, and export and strong ales still more. The average amount used in the United Kingdom in 1914–15 was 1¾ lbs. per barrel. Lager beer brewers use about ¾ lb. hops per barrel.

Boiling with hops destroys the enzymes of the wort, increases the acidity, precipitates coagulable albuminoids, hydrolyses some constituents, increases the wort constituents by the addition of the soluble portions of the hops, sterilises the wort, and darkens the colour, probably due to aëration causing oxidation.

The hydrogen ion potential increases by boiling with 1 lb. hops per barrel from 6 to 5·5, and to 5 if 2½ lbs. per barrel are added.

Proteid coagulation reaches its maximum after 4 hours boiling, about 5 p.c. of the total nitrogen is thus precipitated; the greater the amount of hops the greater the amount of coagulation, but as the hops contribute nitrogenous compounds, the total amount of nitrogenous bodies in the wort is not much affected.

After boiling, the contents of the coppers are emptied into the hop back, a vessel furnished with a false bottom of perforated plates by means of which the hops are strained from the wort. The layer of hops acts as a filter, and removes the albuminoids and other matter precipitated by boiling. The hops remaining are either extracted with hot water or pressed dry in a hydraulic press, the spargings or pressings, as the case may be, being added to the remainder of the boiled wort. The spent hops were formerly used as a manure, but now (1918), owing to the scarcity and high price of feeding stuff, are used as cattle food, either fresh from the brewery or usually dried and ground and incorporated with other materials. The dried hops contain 22 p.c. proteins and 35 p.c. assimilable carbohydrates (Baker and Hulton, J. Inst. Brewing, 1917, 455). The wort should run off from the hop-back quite 'bright.' It is now allowed to cool. Formerly only large shallow vessels were used, but now these vessels are of varying depth, or are sometimes dispensed with; in any case the wort remains in them only for a short time. The cooling is completed by allowing the wort to flow over refrigerators, vessels in which a current of cold water flows in tubes in the reverse direction to the wort which flows outside the tubes. The cooling stage is of considerable importance, both chemically and biologically.

The wort, during cooling, throws down a deposit, partly due to the separation of calcium oxalate, some of which forms a scale on the cooling vessel, and partly to a separation of minute particles called gluten particles, and which appear to be a compound of proteid and hop tannin (Brown, J. Inst. Brewing, 1913, 84). This substance contains about 10 p.c. nitrogen, it is easily soluble in alkalis, and is reprecipitated by a trace of acid. It not only separates during cooling, but continues to deposit more or less during all subsequent stages of brewing and storage. Although its total amount is small, never reaching more than 1 p.c. of the nitrogen compounds, yet owing to its liability to form opalescent suspensions, it is of considerable importance. Agitation whilst cooling from 49° (120° F.) to 27° (80° F.) is found to cause flocculation of these particles.

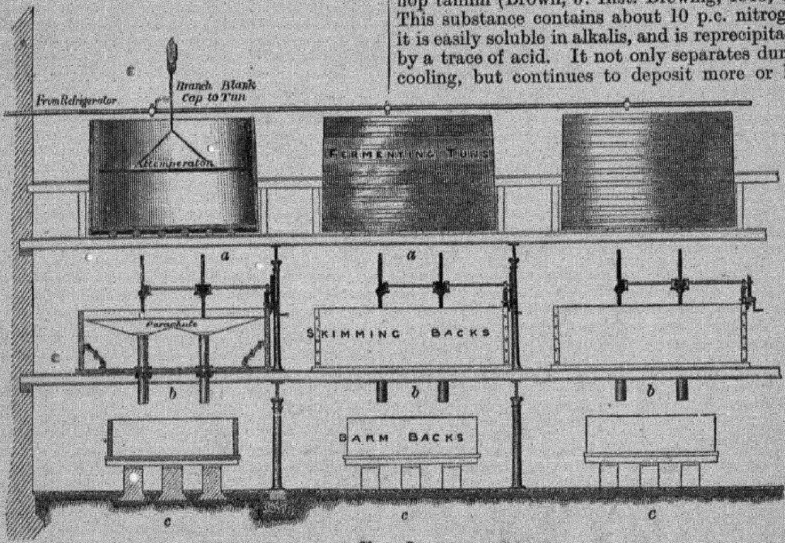


FIG. 9.

During the cooling process, the wort absorbs oxygen from the air. From experiments it appears that from 5 to 7 c.c. oxygen may be absorbed per litre of wort, the latter figure indicating full saturation.

The wort also usually becomes infected during cooling. Until the temperature falls below 55° C. (130° F.) there can be no infection; so for this reason coolers are sometimes dispensed with, and the worts run direct from hop back to refrigerator and thus rapidly cooled. This is effectual in reducing infection, but it has been found sometimes to lead to clarification trouble, which appears to be due to the separation of the above-mentioned gluten bodies in such a minute state that they will not deposit. In general some kind of cooler is used, either a shallow or deep vessel.

Infection on the cooler and refrigerator must be initially due to air infection, and proposals have been made to supply the rooms in which these are placed with sterilised air. In practice it is found, in all but exceptional cases, that the amount of air infection is very small compared with the amount of vessel infection. If the coolers are made of metal there should be little difficulty in keeping these sterilised, as the hot wort every time it covers them should do this; if they are wood it is found that, however well made, sterilisation is impossible. Owing to its porous nature organisms live in the pores just below the surface, and the non-conducting nature of the wood prevents any but the immediate surface layers rising to the sterilising temperature.

The refrigerators, with the necessary pipe connections, are metal, and it appears at first that there should be no difficulty in keeping these sterile, but owing to crevices at joints, &c., in practice complete sterility is impossible to attain.

With care, a harmful amount of infection can be avoided, and air sterilisation, although it may be looked on as a counsel of perfection, rendered unnecessary. If, however, precautions are not taken, the cooled wort may be very grossly infected.

The wort runs from the refrigerator at a temperature of 15°–16° (60° F.) or thereabouts, according to the time of the year and kind of beer, into the fermenting vessels. For lager beer, however, the wort is cooled to 5°–7° (40°–45° F.).

The fermentation vessels are made of wood, metal, stone, slate, concrete, &c. Metal may be considered the ideal material, as its surface is impervious, and it is easily sterilised. They are usually either circular or rectangular with flat bottoms; circular vessels have no corners in which dirt can accumulate, but rectangular vessels make more use of the often limited space.

As soon as the collection begins the wort is 'pitched,' *i.e.* is seeded with a yeast derived from a previous brewing. The number of yeast cells added is very much greater than the number of organisms with which the wort is normally infected. The amount, however, must be so regulated, according to the nature of the wort, that a considerable increase (5–10 times) is possible. The yeast '*Saccharomyces cerivisiæ*,' used by brewers, is a 'culture' yeast, that is, one which has been selected or possibly evolved in civilised communities as specially suitable for brewing.

There are two main varieties, 'high' or 'top' fermentation yeast, and 'low' or 'bottom' fermentation yeast.

The first is used at a higher temperature than the second; the brewery fermentations are consequently more rapid; the yeast rises to the top towards the end of the fermentation, whereas, under the conditions in which the latter is used, it falls to the bottom at the end of the fermentation. Lager beer is brewed on the low fermentation system; all other beers and stouts on the high fermentation system.

As worts usually become infected by other yeasts (wild yeasts) and bacteria during the cooling and subsequent processes, the yeast crop obtained at the termination of fermentation will contain foreign organisms. As this is used for seeding the succeeding worts, it is easily possible in time for the seed yeast to become seriously infected, even if the initial wort infection is kept down by suitable precautions. As will be seen later, these foreign organisms may lead to serious defects in the final product.

In order to surmount this difficulty, Hansen, in 1883, introduced his pure yeast system into bottom fermentation breweries He separated single yeast cells from the brewery yeast, and from each of these grew sufficient to make a trial brewing. The culture giving the most satisfactory result was selected and used in the brewery. A pure pitching yeast was thus obtained. This has been adopted with great success in lager beer brewing, but breweries working on the top fermentation system have not found the pure yeast thus prepared altogether satisfactory. Many reasons have been given for this. Although there seems to be no doubt that in some breweries, notably in Denmark and America, top fermentations are carried out successfully with a pure yeast; yet in many other breweries in which it has been tried, it has been abandoned. It is fairly well agreed that the explanation of its non-success is that a mixture of yeast is necessary in this case, although there is much diversity of opinion as to what this mixture should be (Claussen, J. Inst. Brewing, 1904, 308; Van Laer, *ibid.* 1894, 55; Siau, *ibid.* 1906, 118; Schionning, C. R. Lab. Carlsberg, 1908, 138; Morris, 1900, 333). Yeast may be freed from bacteria by treatment with solution of definite acidity (about 0·1 p.c. H_2SO_4) (Brown, J. Inst. Brewing, 1916, 328).

Fermentation by growing yeast cells is a complicated process, in which numerous chemical reactions take part. Although our knowledge of these is far from complete, yet many important factors have been determined. It is considered that only the hexose sugars are fermentable, the *di*-saccharides being first transformed into their constituent hexoses by enzymes, cane sugar by invertase, maltose by maltase. The rate of fermentation of glucose and levulose is independent of the concentration, except in very strong or very weak solutions; it is proportional to the amount of yeast.

The amount of yeast present in the fermenting wort at any time depends on many factors. If a small yeast seeding be introduced into wort, the yeast grows unrestrictedly until the concentration is sufficient to cause considerable chemical changes in the wort; the yeast growth is then slowed.

During the period of unrestricted growth the number of yeast cells increases logarithmally with the time; that is, over equal intervals of time (generation time) the number of cells double themselves. Brewers' yeast growing unrestrictedly at 20° C. has a generation time of three hours. Temperature has a great influence; between the limits at which yeast grows freely, 5° C. increase causes the rate of growth to be doubled. Carbon dioxide retards the rate; saturation with this gas halves the rate of growth. Alcohol over 2 p.c. retards the rate of growth, the amount depending on the temperature as well as the concentration. Air (oxygen) is necessary for yeast growth. Brewery wort naturally contains dissolved air, and oxygen combined with some wort constituent can also be used by the yeast. Half-fermented wort, saturated with carbon dioxide and prevented from absorbing oxygen by a covering of this gas, is deficient in oxygen necessary for yeast growth. The amount required is small. H. T. Brown estimates that 1·7 c.c. oxygen is necessary for the growth of 10^{10} yeast cells (about 2½ grams pressed yeast). Yeast growth also depends on the chemical composition of the wort. There must be present a carbohydrate, suitable nitrogenous substances such as are produced during the germination of the barley for the purposes of the growing embryo, and phosphates, potassium, calcium, and magnesium salts (A. J. Brown, Chem. Soc. Trans. 1905, 1395; H. T. Brown, J. Inst. Brewing, 1909, 169; and Annals of Botany, 1914, 197; Stern, Chem. Soc. Trans. 1899, 201; and 1901, 943; Slator, *ibid.* 1906, 128; 1908, 217; Biochem. J. 1913, 197; J. O'Sullivan, Chem. Soc. Trans. 1892, 593, and 926).

The changes which take place during the

fermentation of a brewery wort are briefly as follows: An average seeding (pitching) of 10 million cells per cubic cent. will increase up to about 100 million per c.c. There is a period of quiescence before growth starts. It then proceeds steadily, but retarding influences soon come into action and continually slow down the rate. The chief of these is the effect of carbon dioxide and the gradual failure of the oxygen supply. There is plenty of yeast food present, and the amount of alcohol is not sufficient to have any great influence. Rapid fermentation is now taking place, with evolution of large quantities of carbon dioxide which prevents air getting into the fermenting solution. It is at this stage of the fermentation that brewers who employ two fermentation vessels (*see* below) usually 'drop' or 'tun,' that is, transfer the fermenting worts from the one vessel to the other. This causes the removal of some carbon dioxide, and allows some air to be absorbed by the worts, there is a slight renewal of yeast growth; but the chief amount of yeast increase has now taken place. The rate of fermentation is now mainly dependent on the number of yeast cells and the temperature.

The influence of temperature is great; the following table gives the grams dextrose fermented per second by 10^{14} yeast cells (Burton yeast):-

Temperature	40° C. .	5·05 grams.
,,	35° C. .	4·05 ,,
,,	30° C. .	3·00 ,,
,,	25° C. .	2·08 ,,
,,	20° C. .	1·30 ,,
,,	15° C. .	0·68 ,,
,,	10° C. .	0·345 ,,
,,	5° C. .	0·140 ,,

The temperature continuously rises owing to the heat evolved by fermentation: the heat of fermentation of glucose is 22K. (Bouffard, Compt. rend. 1895, 357; A. J. Brown, J. Inst. Brewing, 1901, 93), and the brewer has to control this by suitable cooling appliances.

Glucose, fructose, and cane sugar are fermented faster than maltose; maltase is not so abundant in the yeast as invertase. Small amounts of glucose present in half-fermented wort may very likely have come from the maltose; there are also present in malt worts transformation products of starch of higher molecular weight than maltose, and there is some evidence that some of these are fermented.

The mechanism of alcoholic fermentation is still to be discovered, although some facts have been determined. Buchner and his co-workers (1893–98) proved that an enzyme capable of fermenting glucose could be separated from the living yeast cell by great pressure. Harden and Young (Proc. Roy. Soc. 1908, 299; 1909, 336; 1910, 321) have investigated this reaction and established the equation,

$$2C_6H_{12}O_6+2PO_4HR_2$$
$$=2CO_2+2C_2H_6O+2H_2O+C_6H_{10}O_4(PO_4R_2)_2$$

The hexose phosphate may be isolated and its salts prepared; when hydrolysed by acid it decomposes into phosphoric acid and fructose; it is slowly hydrolysed by an enzyme present in yeast juice and the resulting sugar fermented. By filtering the juice through gelatine supported by a porous filter cell, Harden and Young were able to separate the juice into two portions, either of which was itself incapable of fermenting glucose, but which regained this property when reunited. The filtrate containing the co-enzyme can be boiled without losing its activity, but the residue is thermolabile. Harden (Biochem. J. 1917, 1104) found that a mixture of potassium or ammonium phosphate with acetaldehyde or potassium pyruvate can function completely as the co-enzyme. Instead of yeast juice obtained from the living cell by pressure; these reactions can be carried out by Lebedeff's dried yeast (Compt. rend. 1911, 49), or zymin (Albert, Buchner, and Rapp, Ber. 1902, 2376).

How far this important work bears on brewery fermentation it is difficult to say. Fermentation by living yeast is not influenced by the addition of phosphates, and one-half of the sugar is not fermented rapidly and one-half slowly. It seems probable that there are intermediate products between the sugar, and alcohol, and carbon dioxide, and although much work has been done, the theories so far advanced do not carry conviction.

The chief products of alcoholic fermentation are alcohol and carbon dioxide, the amount of alcohol produced according to the simple equation of Gay-Lussac is 51·1 p.c. from a mono-saccharide, and 54·1 p.c. from a di saccharide. The sugars of malt worts consist of about 83 p.c. maltose and 17 p.c. of sugars pre-existent in the malt which are mainly cane sugar, glucose and fructose. H. T. Brown (J. Inst. Brewing, 1914, 693) found there was produced at the commencement of the fermentation 56 p.c. of alcohol (0–1·5 p.c. alcohol) falling to 52·6 p.c. (1·5–3·0 p.c. alcohol) and 51·5 p.c. (3 p.c. alcohol onwards).

Besides alcohol and carbon dioxide there are produced by the fermentation, glycerol, succinic acid (Ehrlich, Bied. Zentr. 1908, 197), and higher alcohols (Ehrlich, Ber. 1907, 1027; Ashdown and Hewitt, Chem. Soc. Trans. 1910, 1636).

A considerable reduction of the nitrogen content of the wort takes place during fermentation. This varies from 20 to 40 p.c. of the total wort nitrogen, according to working conditions. By adding more sugar and again fermenting it is possible to remove nearly 60 p.c., but a further fermentation will only remove a few per cent. more (H. T. Brown, J. Inst. Brewing, 1907, 423).

The hydrogen-ion potential increases during fermentation from 5 to 4 (Luers, Zeits. Ges. Brau. 1914, 79).

The amount of acid produced during fermentation is dependent on the acidity of the wort; within limits, the more alkaline the wort the more acidity is produced; thus the yeast tends to produce a certain favourable concentration of acid (Windisch and Koolman, Woch. Brau. 1914, 225; Moufgang, Brass. et Malt, 1913, 177 and 297; 1914, 72).

If the wort were left undisturbed in the fermentation vessel, the first cauliflower-like foam which forms in a few hours, would give place about two hours later to a larger rocky and glistening foam, and this in two or three days in turn to a yeasty head. Throughout the greater portion of the fermentation, the yeast, which has a higher specific gravity than the wort, is kept in suspension by the rising bubbles of carbon dioxide, but towards the end it flocculates and entangles the rising bubbles of

CO_2, the spongy mass thus formed rises to the surface, forming the yeasty head. If, however, not quickly removed, the gas is lost and the yeast falls to the bottom of the liquid. If yeast be not removed as soon as it rises, but be allowed to fall through the fermented wort (or beer as it now is), it communicates to this a yeasty flavour and spoils it. In bottom fermentation the yeast also flocculates towards the end of the fermentation, which owing to the low temperature proceeds much slower, and the yeast falls to the bottom of the vessel.

The top fermentation brewer, therefore, adopts some system of 'cleansing,' that is, some mode of removal of the yeast as soon as it rises to the surface. There are two typical systems in use, *i.e.* 'the skimming system,' in which the fermentation throughout proceeds in large vessels, and the yeast as it rises is skimmed off; and the 'cleansing system,' in which the latter portion of the fermentation is conducted in casks, and the yeast allowed to work out of the bung hole, the cask being kept sufficiently full by toppings of bright beer. There are many modifications of these two systems.

The skimming system is the one chiefly employed in the United Kingdom, but instead of skimming off the yeast by hand, an apparatus termed a yeast parachute is fixed in the fermenting vessel; this has a funnel shape with the narrow end in communication with a pipe passing through the bottom of the vessel (Figs. 9 and 10).

The height of the aperture is controlled by suitable gearing, so that the yeast as it rises flows over the edge through the pipe into a vessel below. In very large vessels this is assisted by the movement of the board. Attemperators, or coils through which cold water can be circulated, are usually fitted so that the temperature of the fermenting wort may be controlled.

It is usual to commence the fermentation in a plain vessel and 'drop' the wort when about half fermented into the skimming vessel. The effect of this has been described above.

An elaboration of the simple cleansing in casks, is the Burton Union System. This is so totally different from the skimming system that all others may be said to be intermediate, and it is not proposed to describe them.

The beer to be worked or 'cleansed' by the Burton System, is collected and pitched (seeded) in vessels of about 50 barrels capacity, and the fermentation allowed to proceed until the attenuation of the fermenting wort is about two-thirds of the original gravity, and the temperature has risen to 18°–21° (65°–70° F.). The wort is then 'tunned,' that is, transferred to the unions.

A set of Burton Unions (Fig. 11) consists of two rows of casks, each cask holding about 150 gallons, mounted horizontally on trunnions on aframe work. Above the casks is fixed a long shallow trough (the yeast trough), not quite one-half the width of the double row of casks, and at one end of the union set is a smaller cross trough, the bottom of which is a few inches lower than the yeast trough, but high enough to command the casks. Each cask is furnished with a swan neck which fits into a socket in the highest portion of the cask, and projects just over the edge of the yeast trough, and with a tap at the lowest portion of the cask, the nozzle of which projects a couple of inches into the cask. The tap has a screw thread, so that the inlet can be lowered or the tap entirely removed, leaving the cask opening free. The casks are also provided with attemperators through which cold water may be passed for controlling the temperature of fermentation. The yeast trough is also provided with attemperators which are counterpoised in order that they may be easily lifted up.

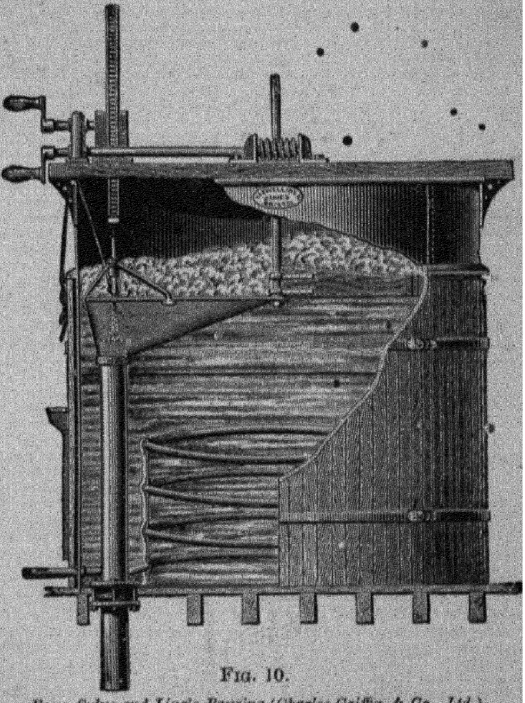


FIG. 10.

From Sykes and Ling's Brewing (Charles Griffin & Co., Ltd.).

At one end the yeast trough communicates with the cross trough or feeder by outlets at various levels, any one or all of which may be closed as required. The feeder communicates with the casks by a long side pipe, the feeder inlet of this having a screw cup which may be raised or lowered, in order to prevent sediment from the feeder getting into the cask, or the cup may be removed entirely. This pipe is furnished with a main tap to control the flow into the cask (the feed), and each cask with a separate tap, so that any one may be disconnected. There are also outlets from the yeast trough and feeder for removing yeast (barm).

The casks, top trough, and feeder are filled with the fermenting wort, but none of the vessels is full of liquid, as there is a considerable amount of foam. The fermenting wort in the cask is under the pressure of the head of liquor in the feeder, and consequently so long as carbon dioxide is being produced in quantity, a foam is forced up the swan neck into the yeast trough. This settles to some extent, and furnishes more head of liquor in the feeder, and so the circulation continues. With a wort of fairly high gravity the whole bulk of the brewing would circulate several times. When the fermentation nears the end, the character of the foam changes, owing to the rise of the yeast. It becomes yeasty, and in the yeast trough separates, a part of the yeast settling to the bottom, and a part forming a thick skin on the surface; in between these two layers is a stratum of fairly bright beer. This bright beer only is allowed to return through the feeder, where a little more settling takes place, into the casks, so that ultimately the casks become filled with more or less bright beer, and the greater part of the yeast remains in the yeast trough. The beer is allowed another day or so in the cask to settle, and it is then run from the bottom tap by a trough into a vessel below (the racking vessel), the tap projecting into the cask sufficiently to hold back the sediment (grounds).

The fermentation is so controlled that at the racking stage there always remains some fermentable sugar; and as whatever mode of yeast removal is adopted, it is impossible to remove all, some remains in suspension. In this state the beer is racked, *i.e.* transferred from the brewery vessels to the carriage casks. It is convenient and usual to employ an intermediate vessel (racking vessel). This is provided with taps, usually of special design, so that the casks are filled without loss due to overflow.

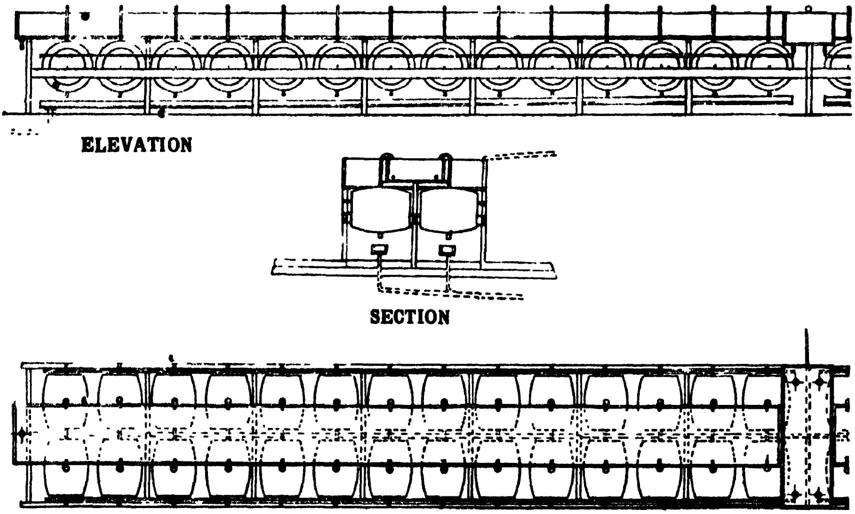


Fig. 11.

Lager beer is not racked into the carriage casks immediately at the conclusion of the brewery fermentation, but kept in cold stores for 2–4 months in lager casks (large vessels holding 100–3000 gallons). During storage a slow after-fermentation takes place, and during the last period the carbon dioxide is allowed to accumulate up to a pressure of 2–4 lbs. per square inch. The beer clarifies, and is racked into casks or bottles for immediate consumption. Stout is also often stored in vats between the end of the brewery fermentation and racking stage.

Several additions are commonly made to the beer when racked direct from the brewery vessels. Hops are usually added, from 2 oz. per barrel up to 1 lb. per barrel for strong or stock ales. Hops of fine flavour are chosen for this purpose, as the hop oil which is lost when boiled in the copper is here retained and adds to the beer aroma. Preservative substances of the hop dissolve in the beer, and the bracts, &c., mechanically assist clarification. Hops contain diastase, which, acting on some carbohydrate constituents of the beer, may produce fermentable sugar, and thus give life or 'condition' to the beer (Brown and Morris, J. Inst. Brewing, 1893, 94).

Sugar solutions are often added at racking, or shortly afterwards. This makes 'condition' certain.

An antiseptic, usually a sulphite, is commonly added. Beer naturally contains some SO_2, this is introduced during the kilning of the malt and drying of the hops; as much as 25 milligrams per litre have been found, but most beers contain only a few milligrams per litre (Bonn, Ann. des Falsifications, 1909, 44); it is also an ancient custom to sterilise the interior of the vessels with sulphur dioxide. When sulphurous acid (or sulphites) is added to beer, a portion is soon oxidised, the remainder combines with the sugars or other aldehydic or ketonic compounds, and in this state is much less toxic than the free acid. Wiley (U.S.A. Dept. of Agriculture, 1907) and Kerp (Arb. aus der Kaiserliche Gesundheitsampte, 1904, 21, 153–284; 1907, 26, 231) have made exhaustive investigations on its toxic action. The moderate use of this antiseptic is generally permitted.

The Beer Materials Committee, 1899, reported that it would be unwise to prohibit preservatives in beer. An International Food Congress, Paris, 1909, recommended that it be allowed up to 85 milligrams per litre. Such an amount has but a slight retarding effect on yeast growth and fermentation, and less is sufficient to prevent the growth of some common beer bacteria, such as *saccharobacillus Pastorianus*, which in the absence of sulphite may do much damage.

An important by-product of the fermentation is the yeast or barm; not so long ago this was a waste product difficult to get rid of, and only used as a manure. Now it is a valuable food, and otherwise useful.

The barm, as separated from the beer, is a thick creamy mass, and is usually pressed in a filter press, the bright beer being returned to the brewery vessels. The filter cake is a cream-coloured powdery mass containing about 75 p.c. water. If allowed to stand, it autolyses and liquefies in a few days by the action of the digestive enzymes it contains; the most satisfactory way to preserve it, is to dry it on steam-heated rollers. The pressed yeast is heated, when it liquefies, and then flows in a thin film on to the hot revolving roller, a current of hot air drives away the steam, and in about three-fourths revolution the film is dry and is scraped off by a fixed knife. Such dried yeast is an excellent food for cattle, but possesses a rather bitter flavour; this may be to some extent removed by washing the pressed yeast before drying with ammonium or sodium carbonate. It contains 5–10 p.c. water, 50–60 p.c. albumenoids, 25–35 p.c. carbohydrates, up to 4 p.c. fat, and about 10 p.c. ash, of which about one-half is phosphoric acid. By some refinements in the preparation a product is obtained resembling meat extract, and largely used in the preparation of dried soups (Petit, Brass. et Malt, 1917, 257). It has been shown to contain water soluble accessory growth-promoting substance; this is not present in meat extracts (Drummond, Biochem. J. 1917, 255).

From brewers' yeast is prepared nucleic acid (Clarke and Schryver, Biochem. J. 1917, 319); this, on hydrolysis, yields phosphoric acid, adenine, guanine, uracil, cytosine, and *d*-ribose. Yeast nucleic acid or its sodium salt is injected subcutaneously with the object of increasing the number of leucocytes. Silver preparations (nucleosil and nargol) are used in inflammatory diseases, and iron salts (fer ascolic and nucleogen) in cases of anæmia. Thyminic acid (solurol) is also prepared from yeast and used for rheumatism and gout.

Brewers' yeast has been used from time immemorial for bread-making. Within recent years its use has been largely supplanted by 'bakers' yeast,' a different variety of *Saccharomyces*, which works at a higher temperature and does not undergo autolysis so quickly. This yeast, although not suitable for brewers use, is employed by distillers. Brewery yeast is, however, improved for bakers' use by passing through a fermentation in a not-hopped (distillers)' wort (Baker, J. Soc. Chem. Ind. 1917, 836). Yeast contains glycogen, as much as 40 p.c. has been found; when used in fermentation estimations yeast must be freed from glycogen by exposing it in thin layers to the air, otherwise there will be a considerable correction to be applied for the auto-fermentation of the glycogen (Henneberg, W. f. Brau. 1902, 781; and Zeit. Spiritusind, 1916, 242). It may be easily prepared from yeast (Harden and Young, Chem. Soc. Trans. 1912, 1928), and at the same time another carbohydrate, the yeast gum of Salkowski (Ber. 1904, 497 and 925) is obtained. This latter yields mannose on hydrolysis. Yeast contains about 2 p.c. lecithine (*di*-palmitoncholine-lecithine). Yeast has a strong reducing power, it reduces sulphur and also sulphites under certain conditions to sulphuretted hydrogen, and under starvation conditions can even reduce sulphates (Stern, Chem. Soc. Trans. 1899, 201; and J. Inst. Brewing, 1899, 399).

The beer racked into the carriage casks is 'shived down.' The residual sugar and yeast react, and the carbon dioxide produced by fermentation super-saturates the beer, and it is now ready for sale. If left undisturbed for a few weeks the beer will normally fall bright. This is not quick enough for ordinary purposes, so it is usual to add 'fining.' Fining is prepared from isinglass, the swimming bladder of various fishes, *i.e.* Acipenser (sturgeon) giving Beluga leaf, Siberian purse, and other Russian isinglass; Polynemidæ giving Bombay, East Indian, and Penang isinglass; Siluridæ (catfishes) giving Brazil lump; and some well-known food fishes as cod, whiting, haddock, and hake giving inferior kinds of isinglass (Bridge, J. Inst. Brewing, 1905, 508). Sole skin is also used. To prepare fining, isinglass is soaked in water acidified with acetic, tartaric, or sulphurous acid, or a mixture of these; it swells up, and more water is added from time to time, until the isinglass is thoroughly 'cut' and a viscous liquid is obtained, from which the undissolved skin is removed by wire sieves. About 3 lbs. of isinglass makes a barrel of fining. From 1 pint to 1 quart added to a barrel causes a coagulation in which both fining and the suspended matter of the beer take part and which soon settles out, leaving the beer bright. If the cask is vented and carbon dioxide is coming off freely, the coagulum is entangled by the rising bubbles of gas and expelled through the vent hole. Fining will not remove actively fermenting yeast or bacteria. It is known that beer colloids carry an electric charge and move to the cathode (Emslander and Freundlich, Zeitsch. physikal. Chem. 1904, 317), and a simple explanation of the action of fining appears to be that the fining colloid carries an opposite charge, and hence, when mixed, the two coagulate.

Isinglass dissolves in hot water, and a solution of gelatine is obtained, which however has no fining action on beer.

The cask of bright beer is now ready for consumption. Cask beer kept 'on tap' more than a few days deteriorates owing to the loss of carbon dioxide and aeration. Bottled beer is free from this risk of deterioration and has advantages of convenience; hence an increasing demand has arisen for it.

If bright beer be bottled, corked, and placed on one side for a few weeks, it will usually be found that a growth of yeast has taken place with fermentation and consequent production of condition in the beer. The yeast easily settles out, and there is usually also a deposit of glutin bodies. This yeast will, as a rule, not be the yeast which has produced the brewery fermentation, and which has also produced the 'condition' which follows immediately on racking, but a wild (secondary) yeast possessing quite different properties, and which has fortuitously obtained access to the beer. The matter fermented corresponds with the composition of a mixture of dextrin and maltose (Morris, J. Inst. Brewing, 1895, 125). This fermentation would, of course, also take place if the beer had remained in cask, and the beer would have become turbid from the growth of the wild yeast; but when growth and fermentation were completed, the yeast would have settled out, leaving the beer again bright, but with an altered flavour. Only beers brewed with good material and a sufficiency of hop remain stable for the length of time necessary for the secondary fermentation and subsequent clarification; inferior and lightly hopped beers fall a prey to bacteria.

The best brands of bottled ale thus produced possess a character and piquancy which is definite and much in demand. Owing to the difficulty of always ensuring the correct amount of fermentable matter and secondary yeasts, and the preparation of a beer of sufficient stability, other methods of preparing bottled ale have been devised.

The most successful is to rack the beer into strong casks or metal tanks and add sufficient sugar, which, when fermented, will produce a considerable pressure of carbon dioxide. This having taken place, the casks containing the beer under pressure are placed in a cold store (if the beer has been conditioned in tank, the beer is forced by air pressure into a similar tank in cold store) and kept at a temperature of 2° (29° F.) for a week or more. The beer, when cooled, should still be super-saturated with carbon dioxide. The cooling causes a precipitation, and in time the beer would fall bright. This would, however, take so long that it is usual to filter the beer through cellulose pulp made up in a filter press. The beer issues from this brilliant, and passes to the bottle-filling machine; in this the pressure is maintained so that no carbon dioxide is evolved, which would cause foaming, and render the regular filling of the bottles impossible. The full bottles are removed from the machine and quickly corked. The beer is ready for immediate consumption, and when raised to room temperature pours out with considerable sparkle, and in this way resembles what may be termed naturally conditioned beer. It has the advantage of being free from sediment, but as the beer is not sterile, this only continues for a few weeks, after which a sediment forms. A considerable loss of colloids takes place during chilling and filtering, and this renders the beer inferior in flavour to beer not thus treated.

It is not usual to pasteurise beer brewed in this country; it keeps sufficiently well for ordinary use, which varies from a few weeks to a few months; strong ale, which is often kept for a year or more, keeps quite well for this time owing to its high alcohol content and hop rate; and export ale will remain stable for years, being brewed from fine malt and large proportion of hops. With lager beer, however, the contrary is the case; if required for export this must be pasteurised, usually at a temperature of 55°–60° (130°–140° F.), and is often so treated for home consumption as it does not keep more than 3–6 weeks at ordinary temperatures.

The chief beer brewing countries are the United Kingdom, the United States of America, Germany, Austria, Belgium, and Denmark. In each country the methods, and consequently the products, differ. The United Kingdom brewers employ mainly the high fermentation system, although a little lager is also produced. The beers are mild, bitter, and stout (porter). The mild ale differs from the bitter in being brewed with less hop, 1 lb. against 2 lb. per barrel for a wort of sp.gr. 1050, and with a higher dried malt giving a sweeter and darker beer.

Stouts and porters are prepared with an intermediate quantity of hops and roasted malt to give the black colour and flavour.

Pale ale is a bitter beer prepared from a wort of sp.gr. 1060 and about 3 lbs. hops per barrel. Strong and export ales are highly hopped, the wort for the former is usually of a sp.gr. 1100, but occasionally beer from worts sp.gr. 1125 has been brewed.

The average original gravity was 1052 in 1914, since then, special war restrictions have reduced this to 1030 (1918).

The average amount of hop per barrel used in 1915 was 1¾ lbs.

The beer duty is levied on the specific gravity of the worts.

German and Austrian brewers employ almost exclusively the low fermentation system. Dark beers are brewed from well-grown high dried malts, and light beer from less grown low dried malts.

In pre-war days very little malt substitute was used in Germany. Berlin white beer is brewed from wheat and barley malt. The gravity of German beers did not materially differ from those of the beers of this country, although the average gravity is lower owing to the non-production of strong ales. The average gravity of Austrian beers is a little more than that of German beers. The war has caused a considerable reduction, beers being now brewed of an original gravity of 1012-1036. The beer duty is levied on the material.

United States brewers employed both high and low fermentation systems, that is, brewed 'ale' and 'beer,' as the products of these two systems were there called. The tendency was, however, for beer (lager) to be the chief product. Rice and maize preparations were used extensively as malt substitutes, and the malt was prepared from a barley of higher nitrogen content than the European brewers would care to use. The duty was levied on the beer produced.

Belgium brewed chiefly top-fermentation beer, but imported considerable quantities of all varieties from the United Kingdom and Germany. Lambic, Faro, and Mars are spontaneously fermented beers prepared from wheat and barley malt, and may take as long as three years to prepare. They have a high acidity. Lambic is prepared from a wort sp.gr. 1065, Mars 1030°, and Faro a mixture of the other two.

In France beer is chiefly brewed in the northern part and mostly by top-fermentation.

Holland brews chiefly top-fermentation beer of rather poor quality, but the brewing of lager is increasing.

Denmark has a highly developed brewing

industry. Both top and bottom fermentation beers of average gravity are produced. The duty is levied on the beer, but that containing less than 2·25 p.c. alcohol is duty free.

Sweden produces half its beer from a wort sp.gr. less than 1024, and this is free from duty; the other half being low fermentation beer of the usual lager type.

The following table gives the average percentage composition of the chief types of beers :—

	Original wort	Unfermented residue	Alcohol	Acidity as lactic acid	Ash	Nitrogen	Phosphoric acid
Pale ale . .	15·4	5·3	5·3	0·1	0·36	0·08–0·09	0·05–0·06
Strong ale . .	24·2	11·2	6·9	0·3	0·55	0·12	0·10
Extra stout .	18·0	7·2	5·7	0·2–0·5	0·33	0·11–0·14	0·15
Mild ale . .	14·0	5·6	4·5	0·09	0·3	0·08	0·06
„ . .	11·0	4·4	3·5	0·09	0·3	0·044	0·038
Light bitter ale .	11·0	3·7	3·9	0·08	0·22	0·044	0·040
Munich lager (dark) .	12·5–15·0	6·6–7·2	3·0–4·1	0·1	0·17–0·27	0·08–0·11	0·065–0·102
Vienna lager .	10–14	4·5–6·5	2·9–3·9	0·15	–	––	
Pilsener . .	11–12	4·5–5·0	3·3–3·7	0·1	0·185	0·062	0·057
American beers (lager) all malt.	12–14	6–8	3–4	0·1–0·2	0·20–0·36	0·08–0·16	0·07–0·13
American beers, 40 p.c. corn, 60 p.c. malt .	11·1–12·6	5·5–6·5	3·1–3·3	0·1–0·2	0·155–0·219	0·05–0·08	0·055–0·064
American ales .	16·7	6·2	5·5	0·2	––	0·073	0·061
Berlin white beer	9–12	4–6·5	0·9–3·6 (av. 2·75)	0·4	0·14	0·046	0·030

Analysis of Brewing Materials and Beers.—*Water* is analysed by methods in common use.

Malt analysis is largely empirical. Official methods have been laid down by the Institute of Brewing (Journal, 1906, 1; and 1910, 529), by Continental Brewing Stations (J. Inst. Brewing, 1903, 594; Zeitsch. ges. Brauw. 1914, 372 and 384). The determinations usually made are :—

Moisture.—As malt oxidises and otherwise decomposes when heated, a definite time and temperature is prescribed for drying.

Extract obtained on mashing. As this also varies with the conditions, the official method must be used to obtain comparable results. It is customary to express the result of extract determination as the specific gravity which would be obtained if 1 quarter (336 lbs.) of malt yielded one barrel (36 gallons) wort. The specific gravity is expressed in 'brewers pounds.' This method of expressing the specific gravity is arrived at by taking the weight of one barrel water (360 lbs.) as unity, and the 'pounds' gravity is the figure obtained by deducting 360 from the specific gravity thus expressed. That is, 1 lb. gravity $=\frac{361}{360}=1{\cdot}0028$; or 3·60 lbs. gravity $=\frac{363{\cdot}6}{360}=1{\cdot}010$. Degrees of specific gravity (*i.e.* the excess over 1000) can be converted into 'brewers pounds' by multiplying by 0·36. Continental brewers express the extract as percentage. To obtain the quantity of matter in solution from the specific gravity, the saccharometer of Balling is largely used; this is graduated according to the following empirical scale :—

Degrees Balling	=Sp. gr.	Degrees Balling	=Sp. gr.
1	1·0040	6	1·0240
2	1·0080	7	1·0281
3	1·0120	8	1·0322
4	1·0160	9	1·0363
5	1·0200	10	1·0404
11	1·0446	15	1·0614
12	1·0488	16	1·0657
13	1·0530	17	1·0700
14	1·0572	18	1·0744

The degrees Balling are supposed to indicate percentages of cane sugar; they certainly do not correspond with the percentage of matter dissolved in malt worts. The tables of Schulze-Ostermann (Zeit. f. d. ges. Brauw. 1878, 248; 1883, 16) are also used extensively and give percentages, and grams per 100 c.c., for malt worts. A set of tables drawn up by Elion (Zeitsch. angew. Chem. 1890, 291 and 321) can lay greater claim to accuracy, and also give an approximation to the percentage solids in beer residues. According to this table, if the excess specific gravity over 1000 be divided by the following factors, the result expresses the grams per 100 c.c. at 15° C. For 25 grams per 100 c.c. factor is 3·97; for 20 grams 3·98; for 15 grams 3·99; for 10 grams 4·00; for 5 grams 4·01; for 1 gram 4·018.

A simple calculation will show that the figures expressing brewers pounds extract, per quarter, per barrel, divided by one of the above factors multiplied by 0·336, will give percentage extract. The factor may usually be taken as 4, so that a malt yielding 90 lbs. extract, contains $\frac{90}{4\times0{\cdot}336}=67$ p.c. matter soluble on mashing.

Colour of the wort or beer is determined by Lovibond's tintometer. Continental analysts employ decinormal iodine solution as the standard for comparison.

Matter soluble in cold water is determined; this is considered to give an indication of the manner in which the germination was carried out.

Diastatic activity, measured by Lintner's method or the modification laid down by the

Institute of Brewing Committee, is a useful indication of the kilning.

Nitrogen is conveniently determined by the Kjeldahl process.

Ash.—The determination of ash by burning in a muffle usually gives low results, owing to the loss of acid radicals, as in sulphates or chlorides. Suitable precautions must be taken to prevent this.

Hops.—The chemical examination of hops has already been referred to.

Malt substitutes, such as maize, rice, and their preparations, and sugars are in general analysed by methods in common use. The extract of starchy material is determined by the addition of a sufficient quantity of malt to convert the starch, and on the same lines as that of malt. The extract yielded by the sugars is usually expressed as 'pounds' extract per 2 cwt. per barrel.

Worts and beer residues are examined for matter fermentable by yeast, the optical activity, and cupric reducing power determined; and these determinations may be interpreted in quantities of dextrin, maltose, and other matter with some approach to probability (Morris, J. Inst. Brewing, 1895, 125).

Beer.—The most important determinations are those of the alcohol and the unfermented residue, from which can be deduced the original gravity of the worts before fermentation. This analysis is treated of in great detail in the Report on Original Gravities by Thorpe and Brown (J. Inst. Brewing, 1914, 569), and on this is based the official table used for revenue purposes, and which is given here:—

Spirit indications	Corresponding degrees of gravity lost
1	4·25
2	8·50
3	12·90
4	17·30
5	21·85
6	26·40
7	31·00
8	35·65
9	40·30
10	45·00
11	49·85
12	54·85
13	59·95

A measured quantity of the beer (usually 100 c.c.) is taken, filtered, and washed into a distilling flask; a condenser is connected and the beer distilled to about four-fifths of its volume. The distillate and residue are each made up to the original volume and the specific gravities taken, usually with a 1000-grain specific-gravity bottle. The table gives the degrees of original specific gravity equivalent to the specific gravity of the distillate. The amount of alcohol contained in the distillate is found from published tables, of which an excellent one appears in the report above mentioned, and is also published separately.

The carbohydrates, nitrogen, ash, and colour of beer are estimated in the same manner as indicated above for malt worts.

Preservatives.—Methods for the estimation of preservatives in beer are given in Bulletin 65 of the United States Dept. of Agriculture, 1901, and circular 33 of the same, March, 1907. The most common is sulphurous acid; it cannot be estimated by direct titration with iodine, as the sulphurous acid is in a fairly stable state of combination; but an approximate titration may be made by first decomposing with alkali, then acidifying and titrating (Ripper, J. pr. Chem. (2), 46, 428). The most satisfactory method is to acidify with phosphoric acid, distil in a current of carbon dioxide, and receive the distillate in a solution of iodine, the sulphuric acid formed is weighed as barium sulphate.

Salicylic acid may be detected by extracting a concentrated and acidified beer residue with a mixture of petroleum spirit and ether. The ethereal solution is drawn off, and evaporated. The residue dissolved in water gives the well-known violet colour with dilute ferric chloride if salicylic acid is present. If saccharin is present, this would be extracted at the same time, and recognised by its intense sweetness. Boric acid, fluorides, benzoic acid are occasionally added. Complete details of beer analytical methods will be found in W. Windisch, Das. Chem. Lab. des Brauers, Berlin, 1907.

Characteristics and Defects of Beer.—Beer should have a pleasant flavour and aroma, be super-saturated with carbon dioxide, and when poured into a glass be bright with a persistent foamy head. Beer defects caused by the absence of these characteristics may be due to chemical or biological causes, or a combination of both. Bacteria are often a cause of defective beer, slight changes in acidity have a marked effect on the susceptibility of the beer, slight increases in acidity making it more, and slight increases in alkalinity less, stable.

Aerobic forms such as the ordinary acetic acid bacteria do not grow in beer charged with carbon dioxide. One of the most common causes of spoilt beer is *Sarcina* (*Pediococcus cerevisiæ*), this causes turbidity and acidity. Another bacteria causing a silky appearance and production of acidity is *saccharobacillus Pastorianus.* Ropiness is another defect caused by bacteria; there are several bacteria which can cause this, usually not much acidity is produced, nor is the beer necessarily turbid. The composition of the substance which gives the viscosity is $C_6H_{10}O_5$ (A. J. Brown, Chem. Soc. Trans. 1886, 432; Lafar, Technical Mycology, transl. by C. T. C. Salter, London, 1898, 1910).

Wild yeast or torula growing in beer will usually produce turbidity, and sometimes unpleasant flavour and smell. This, however, is by no means always the case, and if bacteria do not obtain access to the beer, when the yeast growth is completed, it settles out and leaves the beer bright with an altered, but possibly improved, flavour.

An unpleasant bitter flavour is produced by the culture yeast if the greater portion be not promptly removed at the termination of the primary fermentation. This is due to the cell contents passing into the beer.

If beer be infected with bacteria and wild yeasts, it does not always happen that these organisms grow and spoil the beer. Much work has been done to determine the conditions which influence this. H. T. Brown (J. Inst. Brewing, 1916, 344), in a review of our present knowledge, concludes that the composition of the beer has no influence on its liability to wild yeast growth; but that allowing for the bactericidal influence of hops, there is some relation between the total nitrogen content and its liability to bacterial disease. It is disappointing that the large amount of accumulated knowledge has not been of more assistance to the brewer in avoiding these troubles. We are led back to the work of Pasteur and his followers, to the pre-eminent importance of mycology to the brewer.

Beer turbidity is often caused by the so-called gluten bodies referred to above, separating out in such a minute form as not to settle. This is often the case with pasteurised beer. Wallerstein (U.S. Pat. 995820) suggests the addition of a proteolytic enzyme to degrade these bodies, and this has been found efficacious in some cases. This form of turbidity is closely connected with the chemistry of the colloids of beer. These bodies play an important part in the production of flavour and foam retention. They may be poisonous to yeast and also affect the stability of beer towards bacteria. Little is known of their properties, but a statement of the present stage of our knowledge will be found in the Report on Colloid Chemistry, Brit. Assoc. 1917. A. L. S.

BRIDELIA BARK or ASDUANA. The bark of *Bridelia montana* is a useful Indian astringent (Dymock, Pharm. J. [3] 7, 309).

BRILLIANT ARCHIL, -AZURINE, -BLACKS *v.* AZO- COLOURING MATTERS.

BRILLIANT CONGO, -CROCEÏN, -DOUBLE SCARLET, -GERANINE *v.* AZO- COLOURING MATTERS.

BRILLIANT COTTON BLUE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BRILLIANT GREEN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

BRILLIANT ORANGE, -PONCEAU, -PURPURINE, -SCARLET *v.* AZO- COLOURING MATTERS.

BRILLIANT YELLOW *v.* AZO- COLOURING MATTERS.

BRIMSTONE *v.* SULPHUR.

BRINDONIA INDICA *v.* GARCINIA INDICA.

BRIQUETTES *v.* FUEL; also PITCH.

BRITANNIA METAL. Is an alloy of variable composition, usually containing only tin and antimony, although brass and bismuth are sometimes added.

An alloy consisting of 9 parts of tin and 1 part of antimony is attacked slightly by solutions of common salt, potassium, ammonium, and magnesium chlorides, potassium sulphate, potassium nitrate, and sodium carbonate. Caustic soda has a more marked action (Dingl. poly. J. 221, 259).

This alloy is used in the manufacture of teapots, spoons, and dish-covers.

Articles made from it may be coloured by heating them for 15 to 30 minutes in a bath made by mixing 2 lbs. of water, 1½ oz. of cream of tartar, ½ oz. of tartar emetic, 2 oz. of hydrochloric acid, ½ lb. of pulverised zinc, and 1 oz. of powdered antimony. This gives them a brilliant lustre.

By heating in a bath composed of 1 part tartar emetic, 1 part cream of tartar, 3–4 of hydrochloric acid, and 3–4 of ground antimony, the following tints may be obtained: golden, copper-red, violet, and blue-grey.

A metallic ring can be given to articles made of Britannia metal by heating them in an oil-bath to 220° and then cautiously raising the temperature to below 3° above the fusing point of the alloy. Small articles must be kept at this temperature for from 15 to 30 minutes, large articles for one hour; the bath is then allowed to cool. The rapidity of the cooling seems to have no appreciable effect (D. Ind. Ztg. 1867, 507) (*v.* ANTIMONY).

BRITISH GUM *v.* DEXTRIN.

BROCHANTITE. A hydrated basic copper sulphate, $CuSO_4{\cdot}3Cu(OH)_2$, forming bright-green orthorhombic crystals, found in Cornwall, Urals, &c. It is largely present in some of the Chilean copper ores. L. J. S.

BRÖGGERITE. A crystallised variety of the mineral pitchblende (*q.v.*) or uraninite, found as small, isolated octahedra and cubo-octahedra in the felspar quarries near Moss in Norway. It contains about 80 p.c. uranium oxide, together with thorium, lead, &c. *Cleveite* is a very similar, or identical, mineral found in the felspar quarries near Arendal in Norway. L. J. S.

BROMAL. Tribromacetaldehyde CBr_3CHO. Prepared by passing bromine into a solution of paraldehyde in ethylacetate (Pinner, Annalen, 179, 68), or by passing bromine into absolute alcohol, fractionally distilling the product, and treating the fraction boiling at 165°–180° with water. The bromalhydrate thus formed is decomposed on distillation into bromal and water (Schäffer, Ber. 1871, 366; Löwig, Annalen, 3, 288). Bromal is an oily liquid boiling at 174° (760 mm.); sp gr. 3·34. Alkalis decompose it on heating into bromoform and a formate.

Bromalhydrate $CBr_3CH(OH)_2$. Crystallises from water in colourless monoclinic prisms containing one molecule of water of crystallisation, m p. 53·5°. It is less soluble than choralhydrate (Pope, Chem. Soc. Trans. 1899, 460).

Bromal alcoholates. Bromalethylalcoholate is a crystalline solid, m.p. 44°; readily soluble in alcohol, sparingly soluble in water (Schäffer, *l c.*). Étard (Compt. rend. 114, 753) has described the action of bromine on various alcohols with the formation of different bromal alcoholates.

The following condensation products of bromal have been prepared: *Bromalammonia* (Schiff and Tassinari, Ber. 1877, 1786); compound with *hexamethylenetetramine* (Lederer, Eng. Pat 17693; J. Soc. Chem. Ind. 1897, 1039); compounds with *formaldehyde* (Pinner, Ber. 1900, 1432); *bromaldiacetate* (Grabutti, Gazz. chim. ital. 1900, 30, ii. 191); *bromalglycolate* (Gabutti, Chem. Soc. Abst. 1902, i 261); and *bromalchloralcarbamide* (Kalle and Co., Chem. Soc. Abstr. 1902, i. 429).

BROMALBIN. A bromine derivative of protein.

BROMALIN. Trade name for a combination of hexamethylenetetramine with ethyl bromide used in the treatment of neurastheni and epilepsy (*v.* SYNTHETIC DRUGS.

BROMBENZENE *v.* PHENYL.

α-BROMCARMINE and β-BROMCARMIN *v.* COCHINEAL.

BROMEIGON. Trade name for an albumi preparation containing bromine.

BROMELIA. Trade name for β-naphthylethyl ether.

BROMETONE. Trade name for tribromo-*tert*-butyl alcohol $CBr_3{\cdot}C(CH_3)_2{\cdot}OH$. Used as a sedative and anæsthetic in sea-sickness, vomiting, chorea, &c.

BROMINE. Symb. Br. At. wt. 79·92. An element belonging to the class of the halogens, and the only element, other than mercury, which is liquid at ordinary temperature and pressure; discovered by Balard in 1826. Name from *βρῶμος*, a stench. Never found free; chiefly in combination with alkalis and alkaline earths. As AgBr, brom-argyrite or bromite, also as embolite in isomorphous mixtures with AgCl in Mexico, Chile, Honduras, in some Silesian zinc ores, and in Chile saltpetre. In sea water, in many marine plants and animals, and in many saline springs. Bromine, as bromindigo, has been found to be secreted by certain species of *Murex*, and is an essential constituent of the Tyrian purple of the ancients. Traces of it are occasionally to be met with in coal, and hence in gas liquors.

Bromine is contained in sea water in the ratio of 0·3 gram Br to 100 grams Cl. Water from the Dead Sea contains 3 grams of Br to 100 grams Cl. Some marine brines analysed by Hicks gave the following results in grams per litre:

Sp. gr.	Total solids	Cl.	Br.
1·141	17·00	124·6	1·3
1·194	24·01	176·9	1·7
1·193	22·04	171·8	1·6
1·221	26·42	202·9	2·2
1·143	18·40	128·7	0·6
1·168	21·10	154·1	0·7
1·171	22·10	159·3	0·3
1·202	25·60	189·2	0·7
1·223	26·98	205·8	1·7
1·062	8·38	55·6	0·3
1·066	8·82	58·5	0·4
1·075	9·99	65·7	0·5
1·069	9·27	61·5	0·3
1·057	7·49	50·5	0·4

At ordinary temperatures bromine is a dark brown-red liquid of most irritating smell, very volatile; vapour yellowish-red, and becoming less transparent when heated.

It boils at 63° and solidifies at 73° to a brown-red crystalline mass of semi-metallic lustre and conchoidal fracture. The solidifying point is considerably depressed by chlorine. The specific gravity of liquid bromine is 3·18828, 0°/4° (Thorpe); if free from chlorine 3·10227, 25°/4° (Andrews and Carlton). Coefficient of expansion 0·0011 between 25° and 30°. Specific heat of solid 0·08432 cal., of liquid 0·1071 cal., of gaseous bromine 0·0555 cal.

Latent heat of evaporation at b.p. 45·6 cal., critical temperature 302·2°. Vapour pressure:—

°C.	mm. Hg	°C.	mm. Hg
−80·0	0·13	1·8	67·3
−59·9	0·79	4·0	77·3
−41·3	2·89	4·95	82
−19·4	16·7	5·95	86·5
−10·05	35·0	7·90	95
−7·1	44·5	9·95	104
−0·15	62	12·55	119
16·40	139	34·7	314
18·15	152·5	39·6	378
20·6	172	45·6	478
22·65	190	49·8	553
25·05	212	54·7	658
29·8	239	59·5	768

Solubility of bromine in water (Winkler):—

Temp.	1 part Br is dissolved in parts H_2O	100 parts H_2O dissolve parts Br	100 parts Br water contain parts Br
0·00	24	4·167	4·00
10·34	26·74	3·740	3·62
19·96	27·94	3·578	3·46
30·17	29·10	3·437	3·33
40·03	29·02	3·446	3·34
49·85	28·39	3·552	3·41

The solubility of bromine in water is influenced by the presence of chlorine.

If 1 litre contains

5	10	15	20 grams Cl

it dissolves

46	56	55	54 grams Br

respectively. Solubility in the presence of 1 mol.—

Na_2SO_4	24	NH_4Cl	82·2
$(NH_4)_2SO_4$	77·7	$NH_4C_2H_3O_2$	340·5
NaCl	55·9	KBr	88·5

grams Br per litre.

The specific gravity of bromine water containing:—

Parts Br per litre	Sp. gr
10·72	1·00901
11·68	1·00931
12·05	1·00995
12·31	1·01223
19	1·01491
20	1·01807
31·69	1·02367

The vapour pressure of bromine water with liquid bromine as bottom body:—

Temperature	mm. Hg
0·0 °C.	68
2·0	76
3·0	80
3·95	83
4·95	88
5·95	92
6·2	93
6·95	96
7·95	101
10·0	110
12·5	124
15·9	146

Bromine water when cooled deposits bromine hydrate in hyacinth-red octahedral crystals. Girau (Compt. rend. 1914, 159, 246) proposed, in the place of the composition $Br_2,10H_2O$ usually given (Löwig), $Br_2,8H_2O$ on the strength of thermo-chemical and analytical data.

The solubility of water in bromine is uncertain; according to Wildermann 100 mol. Br dissolve 0·4 mol. H_2O. Of technical importance is the solubility of bromine in the final mother liquors of bromine manufacture:

At	2	10	20	30	40	50	55°
	64·4	64·0	63·6	63·2	60·8	60·0	58·4

grams Br are soluble in 1 litre.

Bromine is very soluble in alcohol, ether, carbon disulphide, chloroform, carbon tetrachloride, hydrogen chloride, arsenic chloride, sulphuryl chloride, sulphur dioxide. Sulphuric acid dissolves traces only. It is miscible with liquid chlorine and appreciably soluble in compressed gases, particularly oxygen, which at 300 atm. holds 6 times the quantity with which it is saturated at ordinary atmospheric pressure.

Bromine is opaque to X-rays; the degree of opacity of bromine compounds is in direct proportion to their percentage of Br. Bromine acts violently on hydrogen, sulphur, phosphorus, arsenic, antimony, tin, aluminium, the heavy metals, and potassium; but it does not react with sodium or magnesium even on heating to 200°. It combines with unsaturated organic compounds and acts as a bleacher and disinfectant. Its vapour acts on the mucous membrane and occasions great irritation, and has been used, therefore, in gas warfare.

Extraction and Manufacture. — Bromine occurs in nature principally, and so far as its industrial preparation is concerned, exclusively in the shape of bromides, accompanying in small quantities the chlorides of sodium, calcium, and magnesium. Its quantity is never large enough to admit of its being prepared directly from the raw material, but where the latter is in the first instance worked for sodium chloride and other salts, the bromide accumulates in the mother liquors, and can be recovered from these. Thus Balard discovered bromine in the mother liquors obtained on making common salt from sea-water, and for many years it was prepared from the mother liquors of the saltworks at Kreuznach, Schönebeck, Neusalzwerk, and other places in Germany. It was also found in 1846, by Alter, in similar mother liquors in America, especially in those at Natrona and Tarentum, later on at Pittsburg, Syracuse, Pomeroy (Ohio), and in the Kanawha region in West Virginia (Mason City, Parkersville, &c.).

Manufacture was first begun in 1846 at Freeport, Pa. U.S. Pat. 12077 for the extraction of bromine from brine was taken out in 1854 by Amalie Stieren of Natrona, Pa. The American bromine industry is at present carried on at Saginaw, St. Charles, Bay City, Midland, and Mount Pleasant, Michigan; at Pomeroy, Ohio; Mason, Hertford, and Malden, West Virginia; in all these localities, except Malden, in connection with the salt industry.

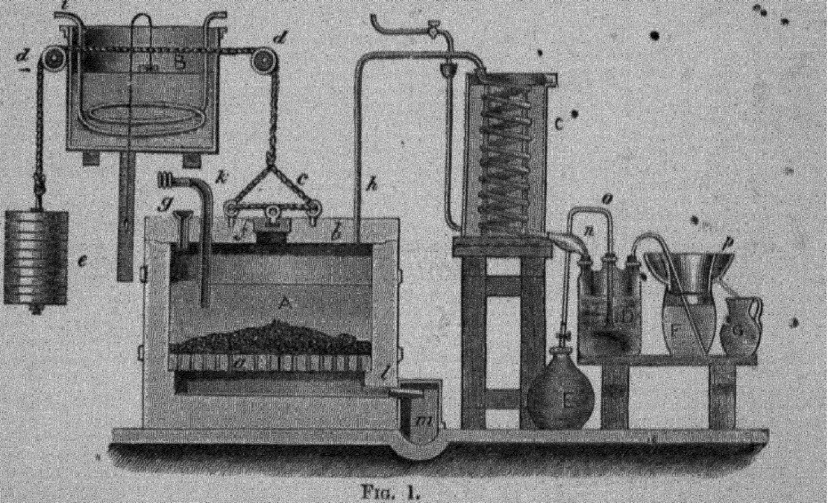


Fig. 1.

Until about 1860 the little bromine that was made was nearly all used for scientific purposes. Then, however, medicine and photography began to demand a greater supply of bromides, and later on the manufacture of coal-tar dyes raised an even more extended demand for bromine. It now became remunerative to recover it in the working up of kelp for iodine, but this yielded only little and impure bromine, and was not long continued. An idea was conceived of recovering it from the water of the Dead Sea, but the project, hardly practicable in itself, was abandoned when Frank had shown that an ample supply of bromine could be obtained from the mother liquors of the Stassfurt potash industry (v. Potassium chloride). He commenced his practical operations in 1865, when he manufactured about 750 kgs. of bromine; in 1867 the output had already increased to 7½ tons, and in 1885 the Stassfurt production of bromine was estimated at 260 tons per annum, the price having gone down from 50 or 60 (sometimes as much as 90) marks per kilogram to 0·75 mark. This lowering of the price was principally due to the fact that since 1868 America had come into the market with bromine made from the above-named saltworks; their liquors contained it in such quantity that they were able to sell much below Stassfurt prices.

The world's production before the war was practically controlled by the 'Associated American Producers,' and the 'German Bromine Convention,' in Stassfurt Leopoldshall.

The rise in price caused by the war gave a new incentive to the American bromine industry. However many of the new producers, after making considerable profits, have abandoned manufacture, and the industry in the vicinity of

Saginaw, Mich., for instance, is now in the hands of a few firms who buy the mother liquors from the other salt producers.

Chemical Processes.—The raw material worked at Stassfurt, crude carnallite (*v.* POTASSIUM CHLORIDE), contains bromine to the extent of from 0·15 to 0·25 p.c. in the shape of *brom-carnallite* $MgBr_2{\cdot}KBr,6H_2O$, isomorphous with carnallite. In the manufacture of potassium chloride, the magnesium bromide accumulates together with magnesium chloride in the mother liquors, which contain usually about 14 grams KCl, 50 grams $MgSO_4$, 348 grams $MgCl_2$, 12 grams NaCl, 2-4·5 grams Br per litre, and have sp.gr. 1·31. As it is impossible to separate the magnesium bromide by fractional crystallisation, the bromine is always extracted chemically, being replaced by a current of chlorine, according to the equation:

$$MgBr_2 + Cl_2$$
$$MgCl_2 + Br_2$$

The chlorine is either generated within the liquors by means of hydrochloric acid and manganese ore, or it is prepared outside and passed into the solutions, cheap compressed chlorine in steel cylinders being nowadays available for that purpose.

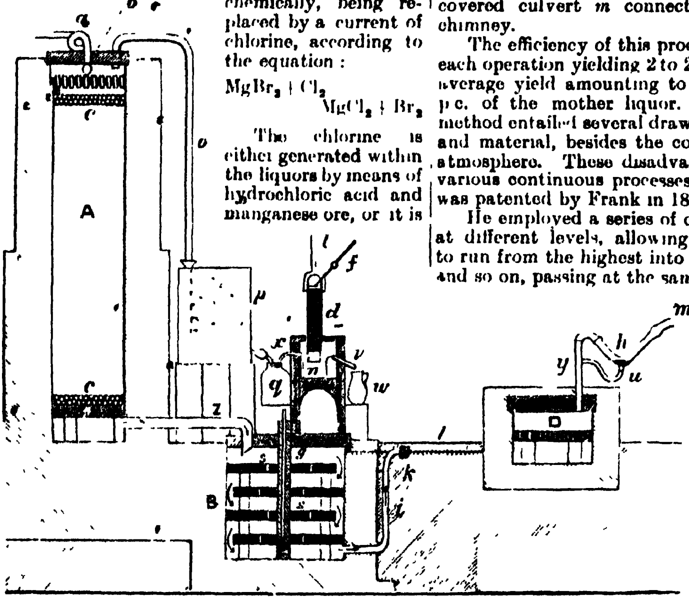


FIG. 2.

In the early days of the bromine industry, the extraction was always done by intermittent working. One of the first apparatus employed was devised by Frank, and is shown in Fig. 1. It consisted of a square vessel or still, A, made of sandstone or slate properly jointed together, of about 3 cubic metres capacity, which was charged with a definite quantity of mother liquor previously heated to 60° in tank B by steam coil *i*; about 200 kgs. of manganese ore, sufficient for several operations, were spread on the false bottom *a*. After closing the man-hole *f*, the required quantity of sulphuric acid of sp.gr. 1·7 was run in through pipe *g*, which was subsequently stopped up with clay, and live steam was passed into the liquor through pipe *k*. The chlorine evolved on boiling acted upon the magnesium bromide present and liberated bromine. This came over pure at first, but above 75° a mixture of bromine, chlorine, and water vapour passed through the lead pipe *h* and the stoneware condensing coil C into the glass bottle D, holding about 8 litres. The distillation was carried on until the pale colour of the vapours in the glass adapter *n* showed that no more bromine was coming over. The condensate separated into a lower layer of bromine and an upper layer of bromine and chlorine water which could be siphoned off through *o* into vessel E, and was added to a subsequent charge. Uncondensed vapours passed into vessel F filled with iron turnings and water, and fitted with a collar, *p*, to allow for frothing, with a run-off into jar G. Each operation, lasting an hour to an hour and a half, was terminated by knocking out plug *l*, and running off the liquor through the covered culvert *m* connected to the factory chimney.

The efficiency of this process was very small, each operation yielding 2 to 2·5 kgs. bromine, the average yield amounting to not more than 0·1 p.c. of the mother liquor. The intermittent method entailed several drawbacks—loss of time and material, besides the contamination of the atmosphere. These disadvantages gave rise to various continuous processes, the first of which was patented by Frank in 1878.

He employed a series of decomposing vessels at different levels, allowing the heated liquor to run from the highest into the next lower one, and so on, passing at the same time chlorine gas generated outside and steam into the lowest vessel, and in counter-current to the higher ones. He thus obtained a steady stream of bromine on the one hand, and a solution of magnesium chloride practically freed from bromine and uncontaminated with manganese salts, on the other. After a time, chlorine was passed into the second lowest vessel, and steam only into the lowest, to free its contents from chlorine before running off. However, the high pressure required to force the chlorine gas through several successive layers of the liquor presented great difficulties in the design and working of this plant. These were overcome by the application of the scrubber principle in the apparatus, patented in 1882 by the Leopoldshall Chemical Works (D. R. P. 19780), and shown in Fig. 2.

The heated mother liquor flows through the water-sealed pipe *a* into column A constructed of stoneware or acid-resisting stone, where it is evenly distributed by pipe *b*. The column is fitted with stoneware balls, *c*, *c* resting on a grating which effects a good contact of the liquor with the chlorine gas ascending through pipe Z. This pipe is wide enough to serve also as outlet for the liquor which runs into the steaming vessel B, provided with a number of superimposed flagstone shelves compelling the liquor to flow in a zigzag course, and finally issues through pipe s. Steam is forced into this vessel by means of a stone pipe *g* and is distributed through perforations in its base. The contents of B, which is always full, are kept boiling, and the steam rises principally through holes in the flagstones, thereby freeing the liquor from chlorine and bromine. The vapours meet the current of fresh chlorine arriving through pipe *l* (shown in dotted lines), which is conveyed through pipe z into the tower A, decomposing the magnesium bromide. The bromine is taken off on top, and passed by pipe *o* through the stoneware condenser *p* into the receiver *q*. The uncondensed vapours are led through *x*, into receptacle *n*, and arrested in the smaller scrubber *d* suspended by rod *t*, and fitted with iron borings, kept moist by a stream of water from tube *f*. The iron bromide collected in *n* is siphoned off through *v* into jar *w*. The regularity of the current of chlorine arriving from *m* is controlled by the amount of water condensing in the bend of the glass tube *h*. If too much water has accumulated, it is blown through the rubber tube *u* into the chlorine washer D. By filling the bend of *h* with water, the current of gas may be interrupted.

Of late years chlorine electrolytically prepared and compressed in steel cylinders has been used, whereby the regularity of the current is under complete control.

The apparatus patented by Wünsche-Sauerbrey (Fig. 3) is based on the same principle as the foregoing. It is, however, technically more perfect and consequently much superior in efficiency.

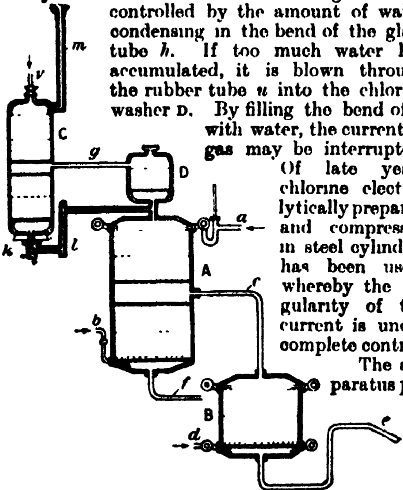


FIG. 3.

It consists of a decomposing vessel A, a steaming vessel B, a condenser C, and an auxiliary condenser D. The four units are built up of cast-iron elements of hexagonal cross-section, lined with stoneware plates and filled with a very large number, several thousands, of specially designed contact bodies (D. R. P. 158715) which rest on gratings of the same material. The four units are so arranged in height that a perfect counter-current is obtained, and in both the decomposer and condenser two centre gratings are provided, in order to keep a free space. The chlorine is passed into the decomposer at *b*, the liquor entering through *a* at a temperature of 65°; after treatment in this unit it runs into the steaming vessel through pipe *f*, where it is freed from chlorine and bromine vapours by means of live steam entering at *d* the vapours passing into the free space of the decomposer. The bromine leaves the decomposer at a temperature of about 95° and undergoes preliminary cooling in the auxiliary condenser D, but is completely condensed in the principal condenser by a stream of water, passing subsequently a bromine and water separator.

The features of this apparatus are the complete recovery of bromine and the thorough utilisation of steam. Although of moderate dimensions, the apparatus is capable, on account of the number and arrangement of contact bodies, to recover 250–270 kgs. bromine from 150 cub. m. liquor in 24 hours. It requires 0·6 kg. chlorine for every kg. of bromine made, and only 3 to 5 kgs. bromine are necessary in the form of iron bromide for the subsequent removal of chlorine from 100 kgs. crude bromine. The cost of production of 1 kg. bromine is 0·45 to 0·50 mark.

Whilst the value of Wünsche's apparatus depends on the most favourable distribution and utilisation of gas and liquor, Kubierschky has designed a plant (Ger. Pat. 194567) in which the counter-current proper is divided into a number of systematically arranged parallel currents, recognising the fact that bromine vapour will be heavier the purer it becomes. As the ratio of the density of water to that of bromine is 18 : 160, a simple upward current cannot possibly yield the best separation, as under currents will always be set up.

The apparatus consists of a single tower column, shown in Fig. 4.

It is lined with stoneware and divided into superimposed compartments, the division plates being liquor-sealed and allowing liquid to pass, but not gas. The compartments are provided with perforated plates *pp* or other contact bodies. Communication between the compartments is established by tubes *rr* so arranged that the vapour always enters from the lower compartment into the upper part of the next higher one, then descends over the plates along with the liquid, and enters the vapour pipe near the bottom, passing through this pipe again to the top of the next compartment, and so forth. The previously heated mother liquor enters at the top of the column, runs down in a direct course and is met by chlorine introduced in the lower part. Steam is passed into the bottom compartment, and follows the course described. The bromine, not subjected to under-currents, issues at *a* from the column and is condensed in an earthenware coil.

Although of extreme simplicity, this apparatus is much superior to all the others, especially in regard to yield, this amounting to from 90 to 95 p.c. of the bromine present in the crude liquors.

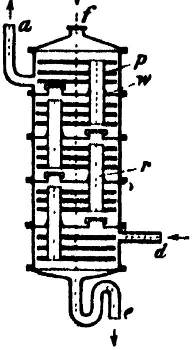


FIG. 4.

The mother liquors, obtained by spontaneous evaporation of sea-water to sp.gr. 1·274 at the salt works of Salin de Giroud, South of France are used for the production of bromide. They are further concentrated to specific gravity of

1·308 and allowed to crystallise during the winter. After removing the magnesium sulphate, bromine is extracted in the following spring by pumping the liquors into vessels of 20 cub. m. each, from which they descend in a regulated stream into stone rectifying columns through which a current of chlorine, from cylinders, and a current of steam ascends. The bromine, after passing through an inclined U-tube and a condensing coil, is separated from the water by gravity, the bromine-water being returned to the column. The crude bromine is rectified by passing steam through it, which carries away the chlorine and part of the bromine. Three units are employed, each of which deals with 50 to 60 cub. m. of mother liquor in 24 hours, and yields about 160 kilos of bromine Forty-four tons of bromine containing only about 1 p.c. of chlorine are thus obtained annually from 15,000 cub. m. of mother liquor. The liquors, after the extraction of bromine, are worked up for potassium chloride.

In America the manufacture is carried on in the majority of works in Ohio, West Virginia, and Michigan, by the intermittent process. The bittern from the main grainers of the salt works is further concentrated to a sp.gr. of about 1·38 (hot), and then passed to the bromine stills. Most of these are made from sandstone quarried at Buena Vista, near Portsmouth, Ohio, where the sandstone is practically free from iron oxide and is of close texture. The shape and construction differ in the various plants, and their working capacity ranges from 400 to 1200 gallons of liquid. Sodium chlorate and sulphuric acid of sp.gr. 1·84 are used in liberating the bromine from the bittern. The use of manganese dioxide and potassium chlorate has been discontinued. Steam is passed into the solution and, as the temperature rises, a reaction takes place approximately represented by the following equation :—

$$3MgBr_2+3H_2SO_4+NaClO_3 \\ =6Br+NaCl+3MgSO_4+3H_2O$$

The bromine set free passes from the still together with any excess of chlorine which is liberated. The bromine vapour is freed from chlorine after passing through washers filled with milk of lime forming calcium chloride and calcium hypochlorite. Some bromine is taken up by the lime, but is recovered later. The bulk of the bromine vapour is condensed in three lead coils arranged in series, each of which discharges the condensate into glass bottles, whilst any bromine passing the last bottle is caught in towers 6 feet to 8 feet high and 2 feet to 2 feet 6 inches wide, made of sewer pipe and filled with coke. The bromine caught beyond the first bottle is usually rather dilute and may be returned to the still. The lead pipes have lately been replaced by stoneware coils in several works. About 35 lbs. of bromine are obtained from 700 gallons of bittern.

The drawbacks of the intermittent process have led to the introduction of continuous processes. The Dow Chemical Company of Midland, Mich., has patented a number of modifications of these.

The chlorine used may be produced chemically or electrolytically within the reacting mass, or introduced from outside. In the place of steam for the removal of free bromine a current of air is used. The bromine is abstracted from the bromine-laden air by chemical re-agents such as iron turnings, lime, sodium bicarbonate, and others. These are worked up for pure bromine or bromine salts by subsidiary processes ; for instance, the ferric bromide solution may be converted into solid ferrous bromide by treatment with further iron.

Electrolytic Processes.—Of recent years, efforts have been made to effect the separation of bromine from the magnesium-bromide liquors by means of electrolysis. A number of processes have been devised by Wünsche, Höpfner, Nahnsen, Pemsel, Rinck, Dow, and Kossuth, but although in some cases plants have been working with more or less success, their introduction has not become general. All but the last-named process employ diaphragms, to avoid secondary reactions. Kossuth works without this, and achieves a great simplicity of plant and working, but at the expense of current required. The yield of electric energy is 40–50 p.c. in his case, and not more than about 70 p.c. in any other method. This low yield is largely due to the extremely small percentage of bromine in the liquors and the consequently large bulk to be dealt with, and to the formation of bromates and chlorates. The formation of solid magnesia is another drawback.

In nearly all the electrolytic methods proposed, the bromine remains dissolved in the solution and must be recovered by the processes described above.

Purification of Bromine.—Crude bromine, as obtained by most of the processes described, contains very small quantities of iodine, cyanogen, bromoform and carbon tetrabromide, lead bromide, and as principal impurity from 1 to 4 p.c. of chlorine as chloride of bromine. The oldest method of purification consisted in agitating the crude bromine with a solution of potassium or ferrous bromide. On account of the frequent breakages of the glass vessels employed, this method was replaced by that of redistillation. In some places glass retorts were used for this purpose, containing about 15 kgs. and heated in sand-baths. Only 3 or 4 charges could be worked in one vessel, and fracture of the retorts was a not unfrequent occurrence. In Stassfurt sandstones stills were and are still employed. These were square troughs with a stone cover, holding about 1 cubic metre. The distillation is carried out in the presence of ferrous or calcium bromide, these liquors being, when used up, added to the original mother liquors. Of late years advantage has been taken of the improved products of the stoneware industry, and stills of this material are largely used. To avoid the occasional cracking of these stills, Mitreiter employs vessels of boiler plate lined with a bromine-resisting material.

The still is charged with 200 litres ferrous bromide solution of 13° to 18°Bé, and about 600 litres crude bromine. The temperature is gently raised by direct steam up to the boiling-point. Double decomposition ensues between chlorine and ferrous bromide, and bromine distils over and is condensed in a stoneware coil, separated from water and then contains only from 0·05 to 0·10 p.c. chlorine.

Pure bromine may be made, according to Barstow, without the aid of steam or heat, by adding sulphuric acid to a mixture of 5 parts of bromide to 1 part of bromate in a cement-lined tub cooled by a lead coil, but kept above the crystallising point of the sodium sulphate formed. The free bromine formed according to the equation:—

$$5NaBr+NaBrO_3+3H_2SO_4 \\ =3Na_2SO_4+6Br+3H_2O$$

can be drawn off from the bottom of the condenser, the yield being 95 p.c. of liquid bromine, whilst the remainder is blown out from the solution with a current of air and recovered with alkali.

In another process, patented by Barstow (Fig. 5), a strong iron bromide solution is fed from tank 2 into the top of a tailings tower, 1, passes through a condensing coil, 3, thence through a re-action column, 4, in which it meets a rising stream of chlorine gas supplied from 5. The mixture of iron chloride and liquid bromine flows downward through the reaction column, and from it through a cooling worm, 7, to a container, 8, where it is separated by gravity. Any vapour formed by the heat produced in the reaction column, or carried away by air, which may be contained in the chlorine gas, is re-condensed in 3 or scrubbed out in tower 1. Any chlorine contained in the crude bromine is removed by agitation with an iron bromide solution, and the bromine retained by the iron chloride solution may be blown out with air and re-absorbed with a solution of ferrous bromide. No steam is used in the process, and the iron chloride can be produced as a commercial solution of sp.gr. 1·32.

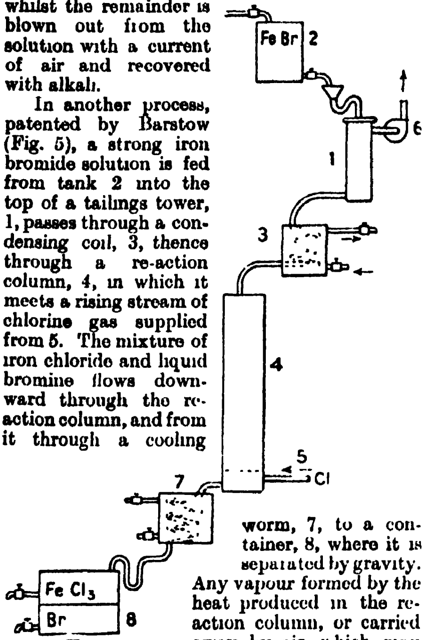


FIG. 5.

Recent processes attempt the purification by rectifying without the aid of chemical agents. Kubierschky (Ger. Pat. 174848) employs in connection with his separating apparatus a refining tower; the crude bromine flows downwards into a vessel charged with bromine and kept at boiling temperature. The chlorine rises in the tower, and the boiling bromine, freed from chlorine, is continually siphoned off and cooled.

The German Solvay Works (Ger. Pat. 205448) have found that in raising the temperature of crude bromine very slowly and keeping it just under its boiling-point, it is possible to free it entirely from its chlorine. The time factor is of great importance for the successful carrying out of their process.

On heating a charge to 59° for 36 to 40 hours, it is possible to remove practically all the chlorine with not much more bromine than corresponds to the composition of bromide of chlorine.

Bromine is sold in strong, white, stoppered bottles, holding 1 litre, and containing 2½ or 3 kilos. The glass stoppers must be well ground; they are secured by pouring some shellac on to the joint, covering them with clay putty, and tying wet parchment paper over all. From four to twelve such bottles are placed in a wooden box, the spaces between being tightly filled with kieselguhr or brown-coal ashes, depending upon whether the bromine is exported or sold for inland consumption.

The principal applications of bromine, whether in the free state or in the shape of bromides, are in photography, in medicine, in the manufacture of coal-tar dyes (especially eosine), and in scientific and analytical chemistry; in the latter it has to a great extent taken the place of chlorine, owing to the greater convenience of its manipulation. A similar substitution has been proposed for many technical purposes. It is used in the extraction of gold and the refining of platinum, and in connection with the manufacture of Prussian blue and potassium permanganate. It is also a disinfectant, and has found some application for this purpose, especially in the shape of *bromum solidificatum* patented by Frank (Ger. Pat. 21644). This is kieselguhr made plastic by means of molasses, &c., pressed into sticks of ½- and ¾-inch diameter, dried, burned to the extent that the sticks acquire a sufficient degree of hardness without losing their porosity, and saturated with liquid bromine in wide mouthed stoppered glass bottles. After the excess of bromine has been poured off, the sticks remain behind, containing about 75 p.c. of the weight of bromine, and are sold in the same bottles. This is a very convenient form of applying it, as a certain number of sticks represent a given weight, and no weighing out of liquid bromine is required.

Bromide of iron is made at Stassfurt and in America, and serves principally as raw material for the manufacture of potassium and sodium bromide. It is a compound of the formula Fe_3Br_8, containing 56-70 p.c. bromine, up to 0·5 chlorine, 18-19 p.c. iron, and 10-15 p.c. water and insoluble matter. The older method for its manufacture consists in passing bromine vapours free from chlorine over iron borings or turnings contained in a cast-iron or stoneware vessel, and kept moist by a stream of water. The solution obtained is passed through a filter cloth or sand filter to remove impurities, notably carbon, and evaporated in cast-iron pans, whereby enough bromine is added to obtain the compound Fe_3Br_8. The brown-red solution is concentrated to a pasty consistency and allowed to cool to a black crystalline mass.

The Associated Chemical Works of Leopoldshall have introduced a method whereby a charge of 1 ton of steel wire and turnings is treated in a closed stone trough with a mixture of bromine vapour and steam in the right proportion. The admission of bromine is so regulated that no bromine vapours are visible through a sight-glass provided on the outlet pipe which is connected to a little scrubber acting as a catch-box. As soon as brown vapours and the falling of the temperature from 170° to 100° indicate a lessening of the activity of the iron, the operation is terminated and the solution run off. Being sufficiently concentrated, the solution obtained in the process may be run direct into the transport barrels, where it is allowed to crystallise.

Bromine salt. In connection with the manufacture of bromine a substance commonly called 'bromine salt' is produced which finds application in the extraction of gold ores. It is practically the mixture $NaBrO_3 + 2NaBr$, and is made by saturating concentrated caustic soda solution with bromine. The solid salt obtained after draining off the mother liquor—which is evaporated—has the approximate composition $1NaBrO_3 + 5NaBr$. To this sodium bromate, electrolytically prepared from bromide, is added, and the mixture finely ground and packed in kegs.

Hydrobromic acid. HBr. *Bromhydric acid*; *Hydrogen bromide.* A colourless pungent gas of irritating smell; fumes strongly in the air. Condenses to a liquid at −73°. May be obtained synthetically by passing bromine and hydrogen through a hot tube or over heated platinum. Best prepared by action of phosphorus and bromine on water, $5Br + P + 4H_2O = H_3PO_4 + 5HBr$; or by the action of a concentrated solution of H_3PO_4 on KBr; or by dropping Br upon melted paraffin heated to 185°.

Gas very soluble in water; weight of normal litre 3·6142 grams; solution when saturated forms a colourless, strongly acid liquid of sp.gr. 1·78, and contains 82 p.c. HBr by weight, corresponding to the formula HBr,H_2O. If the concentrated acid be heated at ordinary pressures, the gas is evolved until the amount of HBr in the solution sinks to 47–48 p.c., when the liquid boils constantly at 126° under a pressure of 760 mm. This proportion of HBr corresponds to $HBr + 5H_2O$, but the liquid is not a true hydrate, since the composition is altered by varying the pressure; thus if the pressure be raised to 1·95 mm., the solution boils at 153° and contains 46·3 p.c. HBr.

The sp.gr. at 15° and p.c. composition of aqueous solutions of hydrobromic acid, is given in the following table (Wright, Chem. News, 23, 242):—

Sp. gr.	HBr p.c.	Sp. gr.	HBr p.c.
1·080	10·4	1·385	40·8
1·190	23·5	1·475	49·5
1·248	30·0	1·515	49·8

For pharmaceutical purposes a dilute solution of hybrobromic acid may be prepared by dissolving 84½ grains of potassium bromide in a fluid ounce of water and adding 9 grains of tartaric acid to the solution. After standing, acid potassium tartrate crystallises out and the solution contains about 10 p.c. of hydrobromic acid. Hydrobromic acid has been used in the treatment of ear complaints. R. L.

BROMINOL (*brominoleum*). Trade name for brominated sesame oil.

BROMIPIN, BROMOPIN. A combination of bromine with sesame oil employed in medicine (*v.* Synthetic Drugs).

BROMITE or **BROMYRITE.** Native silver bromide, found in Mexico and in Chile (*v.*

ω-**BROMOACETOPHENONE** *v.* Ketones.

BROMOCHINOL. Trade name for acid dibromosalicylate of quinine.

BROMOCOLL *v.* Synthetic Drugs.

BROMOFORM. *Tribrommethane* $CHBr_3$. This substance is occasionally met with in the liquid left after the rectification of bromine, in which it occurs associated with *chlorobromoform* $CHBr_2Cl$ (Dyson, Chem. Soc. Trans. 43, 46) and *carbon tetrabromide* CBr_4 (Hamilton, *ibid.* 39, 48).

Preparation.—It may be obtained by mixing 100 c.c. soda lye, 200 c.c. acetone, and 20 c.c. bromine. When the reaction has ceased, 10 c.c. acetone are added to remove the yellow colour of the hypobromite, the layer of bromoform which separates being tapped off and rectified. Yield 75 p.c. (Denigès, J. Pharm. Chim. 24, 243). It may also be prepared by the simultaneous action of bromine and caustic potash on alcohol, of bromine and lime on acetone (Beniger, Amer. J. Pharm. 63, 80); of calcium hypochlorite and potassium bromide on acetone (Fromm, Pharm. Zeit. 39, 164), and by the action of alkalis on bromal. It has been made electrolytically from potassium bromide and alcohol (Fabrik vom Schering, D. R. P. 29771); from potassium bromide and acetone (Coughlin, Amer. Chem. J. 27, 63; and Müller and Loebe, Zeit. Elektrochem. 10, 409), and from calcium bromide, alcohol, and water (Trechcinoki, Chem. Zentr. 1907, i. 13).

Properties.—It is, when pure, a colourless liquid, solidifying at 2·5° and boiling with slight decomposition at 146° under 751 mm. (Wolff and Schwabe, Annalen, 291, 241), at 151°/760 mm. (Thorpe, Chem. Soc. Trans. 37, 1880, 201. Sp.gr. 2·902, 15°/15° (Perkin, Chem. Soc. Trans. 45, 533); 2·8119, 8·5°/8·5° (Thorpe, *loc. cit.*). It is decomposed by potash into potassium bromide, hydrogen bromide, and carbon monoxide, and may be estimated by means of this decomposition (Desgrez, Compt. rend. 125, 780, and Annalen 23, 76; and Richaud, J. Pharm. Chim. 1899, 232). Under the influence of light and air it decomposes, the decomposition products depending on the time of exposure and the amount of available oxygen (Schoorl and Van den Berg, Chem. Zentr. 1906, i. 441). It has been used to a slight extent as an anæsthetic, and in the treatment of diphtheria. Bromoform in water, to which a little alcohol has been added, has been successfully used in cases of whooping-cough complicated with pneumonia (Stepp and Goldschmidt, J. Soc. Chem. Ind. 1890, 213).

BROMOGLIDINE, BROMOGLUTEN, BROMOPROTEIN. Preparations of wheat gluten or vegetable albumin containing bromine used as substitute for alkaline bromides.

BROMOL, BROMOLEIN, BROMOTAN *v.* Synthetic Drugs.

BROMURAL. Trade name for *a-monobromisovalerylurea*. Employed as a hypnotic. Forms white needles, slightly bitter in taste; readily soluble in hot water, alcohol, and ether, sparingly soluble in cold water; m.p. 147°.

BRÖNNER'S ACID, 2-Naphthylamine-6-sulphonic acid *v.* Naphthalene.

BRONZE *v.* Tin.

BRONZE POWDERS. Bronze powders are composed of copper, zinc, tin, and antimony, melted together in the requisite proportions.

In the process of manufacture, the alloy is cast into rods ¼ inch in diameter and 3 feet long. These are rolled until about 2 inches wide, and then cut into lengths suitable for handling. The pieces are hammered out thin, and cleansed by immersion in dilute sulphuric acid. The dried material is then beaten out by steam-hammers until the limit of thickness is reached, when it is cut up by shears into small particles or 'clippings.' These are then pulverised in stamp mills, and the powder sifted, to separate the heavier and better quality powder from inferior material. The latter is mixed with quartz powder and sold very cheaply (J. Soc. Chem. Ind. 1893, 12, 475).

The expense of the above process lies mainly in the production of 'clippings,' which necessitates a great deal of handwork, and a number of methods have been patented for reducing the alloy to a finely divided state by mechanical means. According to one method, the molten alloy is rained into a sheet-iron chamber, in which a shaft carrying blades is rapidly rotated, so as to greatly agitate the air and thereby minutely subdivide the metal at the moment of solidification (Fr. Pat. 331371, 1903). In another, the molten metal flows in a thin film into a receptacle, where it meets a current of compressed air or else a jet of water, the object being to produce bronze foil or leaves (Eng. Pat. 9064, 1903). Methods have also been patented for casting the metal in thin films on the inner surface of a rotating hollow cylinder or in the annular space between two rotating cylinders (J. Soc. Chem. Ind. 1903, 22, 150; Fr. Pat. 335112, 1903).

After the powdered metal has been sifted, the coarser grades are polished in a closed steel cylinder, in which steel wire brushes rub against the walls. When it is necessary to reduce the powder to a finer state of division, it is rubbed with gum-arabic solution, washed and dried at the lowest possible temperature.

Zinc-dust is frequently coated with brass by simple immersion in a copper and zinc cyanide solution, the powder being kept agitated by means of brushes (J. Soc. Chem. Ind. 1894, 13, 893, 958); the product is treated finally in a polishing mill, and used as a bronze powder.

Bronze powders have also been described containing 5–10 p.c. of aluminium, and 0·05–0·1 p.c. of bismuth. The shade of colour is altered by varying the percentage of aluminium, and by heating in air (D. R. P. 44242, 1887).

Few analyses of bronze powders have been published (J. Soc. Chem. Ind. 1910, 29, 1062). 'Gold' and 'bronze' powders were found to contain 70–85 p.c. of copper, and 30–15 p.c. of zinc, together with small amounts of lead, tin, arsenic, iron, and aluminium; 'aluminium' powders consist of nearly pure aluminium; and 'silver' powders contain 77 p.c. of zinc and 21·5 p.c. of aluminium.

Bronze powders are coloured in various ways. One method consists in heating the powder in an open vessel with oil and vinegar, or with wax, paraffin, or oils containing sulphur. Buchner's process consists in shaking the powder in a closed vessel with hydrogen sulphide solution, allowing to stand 24 hours, drying and heating in an oil-bath until sufficiently coloured (J. Soc. Chem. Ind. 1896, 15, 283). Artificial dyestuffs are also used for colouring bronze powders.

The following are examples:—

Colour of powder	Metallic constituents	Total organic matter	Colouring matter
Pink . .	Copper . .	0 3 p.c.	Azine scarlet G
Blue . .	Tin and zinc .	3·8 ,,	Victoria blue 4R
Copper colour	Copper (little zinc)	5·5 ,,	Safranine
Violet. .	Tin (little copper)	3·8 ,,	Fast neutral violet B
Pale green .	Copper and zinc	4·3 ,,	Malachite green
Olive green .	Copper and zinc	5 9 ,,	Brilliant green

Bronze powders are used considerably for printing on textile fabrics. For this purpose they must be mixed with a 'fixer' which allows the powder to be readily applied to the material, whilst so fixing it that brushing will not remove it; the fixer must not, of course, interfere with the brilliancy of the powder. Two classes of 'fixers' are in use, egg or blood albumen, and various varnishes having caoutchouc as their base. In printing such goods, the main point to be observed is that the impression shall be sharp, and applied with sufficient force to prevent the particular fibres from again rising. (For further particulars, *v.* J. Soc. Chem. Ind. 1896, 15, 283; 1900, 19, 243; 1906, 25, 1040; and for various bronze powder substitutes, *v. ibid.* 1896, 15, 284.)

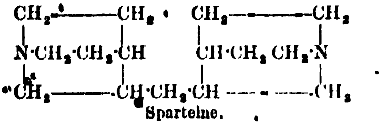
BROOKITE *v.* TITANIUM.

BROOM TOPS. *Scoparii cacumina* B.P. *Scoparius*, U.S. Pat. was deleted in 1916, but *Sparteinæ sulphas* is retained. (*Genêt à balais*, Fr.; *Besenginster*, Ger.). The tops of the common broom, *Cytisus scoparius*, Link = *Spartium scoparium*, L. (Bentl. a. Trim. 70), have been employed for their diuretic action since the Anglo Saxon period, and are noticed in nearly all the herbals and pharmacopœias (Planta genista). The main constituents are sparteine and scoparin

Sparteine $C_{15}H_{26}N_2$, a liquid alkaloid (Stenhouse, Annalen, 1851, 78, 15; Mills, *ibid.* 1863, 125, 71); subsequently shown to be identical with lupinidine from yellow lupin seeds (*L. luteus*) by Willstatter and Marx (Ber. 1904, 37, 2351). It may be obtained from broom tops by extraction with very dilute sulphuric acid, concentration of the extract and steam-distillation of the residue, after addition of alkali. The crude alkaloid may be purified by distillation in a current of hydrogen.

Properties. A colourless liquid, sp.gr. 1·034 at 0°, b.p. 188° under 18·5 mm., or 325° in a current of hydrogen under 754 mm. pressure (Moureu and Valeur, Compt. rend. 1903, 137, 194), 180·5° under 18 mm. (W. and M. *l.c.*). Slightly soluble in water, soluble in alcohol, ether, or chloroform; insoluble in light petroleum or benzene. The aqueous solution is alkaline and very bitter. $[\alpha]_D = -14\cdot6°$ in alcohol (Bamberger, Annalen, 1886, 235, 368), $-16\cdot42°$ (M. and V. *l.c.*) at 20°. Sparteine is a diacidic base, which forms difficulty crystallisable salts. The alkaloid and its salts are toxic.

Reactions and constitution. Sparteine behaves towards alkyl iodides as a ditertiary base, but contains no methyl linked to N (Herzig and Meyer, Monatsh. 1894, 15, 613; 1895, 16, 599; M. and V. *l.c.*). It furnishes no reduction products, and is unaffected by permanganate. Sparteine reacts with methyl iodide to form two monomethiodides, which are regarded as stereoisomerides. On 'exhaustive methylation' sparteine furnishes hemisparteilene $C_{15}H_{22}N$ and trimethylamine and finally sparteilene $C_{15}H_{20}$. On oxidation with chromic acid it yields spartyrine $C_{15}H_{24}N_2$, and eventually oxysparteine $C_{15}H_{24}ON_2$. With hydrogen peroxide dioxysparteine $C_{15}H_{26}O_2N_2$ results, presumably a di-ammonium oxide. From these and other data Moureu and Valeur (Compt. rend. 1905, 141, 261, 328) have assigned the following formula to sparteine—



Sparteine.

The principal papers relating to sparteine are as follows: Ahrens, Ber. 1887, 20, 2218; 1888, 21, 825; 1891, 24, 1095; 1892, 25, 3607; 1893, 26, 3035; 1897, 30, 195; Moureu and Valeur, Compt. rend. 1903, 137, 194; 1905, 140, 1601, 1645; 141, 49, 117, 261, 328; 1907, 145, 815, 929, 1184, 1343; 1908; 146, 79; 1911, 152, 386, 527; 1912, 154, 309; Bull. Soc. chim. 1909, [iv.] 5, 31, 37, 40; and résumé Ann. Chim. Phys. 1912 [viii.] 27, 245-391; Wackernagel and Wolffenstein, Ber 1904. 37, 3238; Willstätter and collaborators, *ibid.* 1904, 37, 2351; 1905, 38, 1772.

For the *salts*, *see* Bamberger (*l.c.*) and Corriez (Bull. Sci. Pharmacol. 1912, 19, 468, 527, 533, 602). The *sulphate* $C_{15}H_{26}N_2$, H_2SO_4, $5H_2O$ is official in the U.S.P., and forms hygroscopic crystals becoming anhydrous at 100° and melting at 153°. Crystals with 3 and with $8H_2O$ have also been described. The salt is soluble in about an equal weight of water, less so in alcohol. It has been recommended as a cardiac stimulant, but its action on the heart is doubtful. Sparteine is much less poisonous than coniine, which it resembles to some extent in action; it also resembles nicotine. For colour reactions of sparteine, *see* Reichard (Pharm. Zentr-H. 1905, 48, 385). The amount present in broom tops varies considerably with the season of the year. There is a well-defined maximum in March and minimum in August (Carr and Reynolds, Pharm. J. 1908 [iv.] 26, 542; Chevalier, Compt. rend. 1910, 150, 1068). The former authors found 0·07 to 1·06 p.c. in commercial specimens, and in specimens from the same locality 0·53 p.c. in March, 0·07 p.c. in August. Chevalier states that the alkaloid wanders into the fruit in the following season, mature seeds containing 1·1 p.c. Valeur (Compt. rend. 1917, 164, 818) has based a method for the estimation on the decrease of solubility in water of the free base with rise of temperature.

Scoparin $C_{20}H_{20}O_{10},5H_2O$, m.p. 202°–219° (according to the rate of heating), is a pale yellow powder separating from the aqueous decoction as a jelly and crystallising with difficulty from alcohol. The formula may be resolved into $C_6H_3{\cdot}OMe(4){\cdot}OH(3){\cdot}C_{13}H_8O_3(OH)_5$, the unresolved portion yielding phloroglucinol on potash fusion, and probably containing a pyrone ring (Goldschmiedt and von Hemmelmayr, Monatsh. 1893, 14, 212; 1894, 15, 360; A. G. Perkin, Chem. Soc. Trans. 1900, 77, 422). Scoparin dissolves slightly in water, readily in alkalis, *e.g.* in ammonia with a deep yellow-green colour. With ferric chloride it gives a violet-blue colour, rapidly becoming dark-brown; it reduces Fehling's solution. Heated with alcohol less soluble isoscoparin, m.p. 235°, is formed, which on solution in alkalis and re-precipitation is reconverted into scoparin. Scoparin is stated to be the cause of the diuretic action of broom tops. G. B.

BROPHENIN. Brom-*iso*-valerylamino acet-*p*-phenetidin.

BROSIMUM GALACTODENDRON (Don.). The latex of this urticaceous tree (cow-tree, milk-tree), growing in Venezuela, approximates to cow's milk in composition. It contains 35·2 p.c. of wax and saponifiable matters, which are used in the manufacture of candles (Boussingault, Pharm. J. [3] 9, 679).

BROUSSONETIA PAPYRIFERA (Vent.). *The Paper mulberry.* The fibrous bark is used in China and Japan for the manufacture of a kind of paper, and in Polynesia in the manufacture of Tapa cloth.

BROVALOL. The borneol ester of *a*-bromo isovalerianic acid $C_4H_8Br.CoOC_{10}H_{17}$.

BROWN, ACID, *v.* AZO-COLOURING MATTERS.

BROWN, ANILINE; BISMARCK BROWN, MANCHESTER BROWN, PHENYLENE BROWN, VESUVINE, LEATHER BROWN, CINNAMON BROWN, ENGLISH BROWN, or **GOLD BROWN;** *v.* AZO- COLOURING MATTERS.

BROWN, ANTWERP, *v.* PIGMENTS.

BROWN, ARCHIL, *v.* AZO- COLOURING MATTERS.

BROWN, BONE, *v.* PIGMENTS.

BROWN, CALEDONIAN, *v.* PIGMENTS.

BROWN, CAPHEK, *v.* PIGMENTS

BROWN, FAST, *v.* AZO- COLOURING MATTERS.

BROWN, FUSCANINE, *v.* AMINOPHENOL.

BROWN, GARNET. The potassium or ammonium salt of *iso*purpuric acid ($C_8H_4N_5O_6K$ or $C_8H_8N_6O_6$). Obtained by Hlasiwetz in 1859 by the action of potassium cyanide on picric acid (Annalen, 110, 289). Forms a dark-brown powder, readily soluble in hot water with red-dish-brown colour. Dyes wool and silk brown in an acid-bath. No longer is use (*v.* also ISOPURPURIC ACID).

BROWN, MADDER, *v.* PIGMENTS.

BROWN, NAPHTHYLAMINE, *v.* AZO- COLOURING MATTERS.

BROWN, PHENYL, *v.* PHENYL BROWN.

BROWN, PICRYL, *v.* PICRYL BROWN.

BROWN, PIGMENT, *v.* AZO- COLOURING MATTERS.

BROWN, PRUSSIAN, *v.* PIGMENTS.

BROWN, RESORCIN, *v.* AZO- COLOURING MATTERS.

BROWN, SOUDAN, *v.* AZO- COLOURING MATTERS.

BROWN, VANDYKE, *v.* PIGMENTS.

BROWN, VERONA, *v.* PIGMENTS.

BROWN BERRIES. The fruit of *Rubus fruticosus.*

BROWN COAL *v.* FUEL.

BROWN HÆMATITE *v.* IRON, ORES OF.

BROWN IRON ORE (*Limonite*) *v.* IRON, ORES OF.

BRUCINE *v.* NUX VOMICA.

BRUCITE. Native magnesium hydroxide, $Mg(OH)_2$, found as platy crystals with perfect micaceous cleavage, or as lamellar masses, in serpentine rocks, at Unst, one of the Shetland Isles, at Texas in Pennsylvania, &c. It sometimes contains a small amount of iron (ferrobrucite) or manganese (manganbrucite). A fibrous variety is called nemalite. L. J. S.

BRUNSWICK BLACK is prepared by fusing 2 lbs. of asphalt, and mixing thoroughly with 1 pint of hot boiled oil. When cool, 2 pints of turpentine are added to the mixture. An inferior but cheaper black may be made by boiling gently together for five hours 25 lbs. each of black pitch and gas tar asphaltum; 8 gallons of linseed oil, and 10 lbs. each of litharge and red lead are then mixed in, and the whole boiled. After cooling, the mixture is thinned by the addition of 20 gallons of turpentine (*v.* also BONE OIL).

BRUNSWICK GREEN. An oxychloride of copper, used as a pigment. Copper filings or turnings are moistened with a solution of salammoniac, and left in contact with the air; the oxychloride so formed is washed off with water, and dried at a gentle heat. The term is also applied to chrome green and to emerald green (*v.* COPPER and PIGMENTS).

BRUSHITE. A hydrated phosphate of lime, $HCaPO_4,2H_2O$, occurring in the guano of Aves Island and Sombrero in the Caribbean Sea.

BRUSSELS SPROUTS. A variety of the cabbage (*Brassica oleracea*), in which numerous small heads are developed along the stalk from the axils of the leaves, instead of one terminal head.

The edible portion contains, according to American analyses:

Water	Protein	Fat	Carbohydrates	Ash
88·2	4·7	1·1	4·3	1·7

(*see* CABBAGE). H. I.

BRYOIDIN *v.* OLEO-RESINS.

BRYONY ROOT. Bryony root has been used medicinally from a very remote period on account of its cathartic properties, and was formerly recognised by several of the national Pharmacopœias, but is now rarely employed. The plants yielding this root are *Bryonia alba*, Linné, and *Bryonia dioica*, Linné (Nat. Ord. Curcurbitaceæ), which are botanically closely allied. They are indigenous to the greater part of Europe, but the last-named species is the only one of the genus commonly found in this country, and, therefore, is frequently designated as English bryony. The roots of the two species are generally considered to possess the same properties, and they appear to be indiscriminately collected, although it has been asserted by Petresco (United States Dispensatory, 18th ed., p. 279) that they differ appreciably in their physiological action. The roots of *Bryonia dioica* contain an enzyme as a light-brown powder, which slowly hydrolyses the glucoside in the root, and also effects the hydrolysis of amygdalin and salicin. The alcoholic extract of the dried root yields a pale yellow essential oil of characteristic odour; a colourless crystalline neutral substance, $C_{20}H_{28}O_5$ (m.p. 220°–222°) $[\alpha]_D$ +58·6°; an amorphous glucoside of a brown colour and bitter taste, which on hydrolysis yields a brown resin, and a sugar forming *d*-phenylglucosazone (m.p. 208°–210°); an amorphous alkaloidal principle, brownish-yellow in colour, and of an intensely bitter taste. From the resin may be prepared (i) a phytosterol, $C_{27}H_{46}$ (m.p. 137°), optically inactive; (ii) a dihydric alcohol, *bryonol*, $C_{22}H_{34}O_2(OH)_2$ (m.p. 210°–212°), yielding a *diacetyl* derivative (m.p. 152°); (iii) a mixture of fatty acids, consisting of oleic, linolic, palmitic, and stearic acids. Bryonol appears to belong to a group of dihydric alcohols of the general formula $_nH_{n-8}O_4$, comprising: *ipuranol*

$$C_{21}H_{38}O_2(OH)_2$$

grindelol $C_{22}H_{36}O_2(OH)_2$, and *curcurbitol* $C_{24}H_{38}O_2(OH)_2$. The *bryonin* of previous investigators consisted of complex mixtures. The activity of bryony root cannot be attributed to a single definite principle, its purgative property resides chiefly in its resinous and alkaloidal constituents (Power and Moore, Chem. Soc. Trans. 1911, 99, 937).

BUBULIN (from *βοῦς*, ox). The name of a peculiar substance, said by Morin to exist in cow-dung, and to be precipitated by metallic salts, tincture of galls, and alum, and therefore to be active in the application of cow-dung to calico-printing.

BUCHU *v.* OILS, ESSENTIAL.

BUCHU or BUCCO. The leaves of three varieties of *Barosma* (ord. Rutaceæ), viz. *B. betulina* (Bartl et Wendl. f.), *B. crenulata* (Hook.), and *B. serratifolia* (Willd.), are known under this name. The leaves are used medicinally by the South African natives.

Their composition has been studied by Brandes (Arch. d. N. Apoth. Ver. 22, 229), Landerer (Buchner's Repert. 84, 63), Flückiger (Pharm. J. 3, 4, 689; [3] 11, 219), Wayne (*ibid.* 3, 6, 723). By extracting the leaves with light petroleum, Bialobrzeski (Chem. Zentr. 1896, ii. 551) obtained chlorophyll, a resin, and an ethereal oil containing chiefly diosphenol, together with a terpene $C_{10}H_{18}$, b.p. 174°–176°, and a ketone isomeric with menthone, and having the constitution $C_{10}H_{18}O$, b.p. 206°–209°; it yields an oxime and a tribrom derivative. After extraction with light petroleum, the leaves, on treatment with cold alcohol, yield 3 p.c. of a brownish-green bitter resin insoluble in benzene, and when the alcoholic extract is treated with sodium carbonate or by other methods diosmin is deposited, forming tasteless, odourless crystals, m.p. 244°.

Semmler and McKenzie (Ber. 1906, 1158) found that the round leaves of *Barosma betulina* yield about 2 p.c. of an oil which crystallises on standing at ordinary temperature; but the long leaves of *Barosma serratifolia* yield 1 p.c. of an oil which remains liquid under similar conditions.

According to Kondakoff and Bachtschiew (J. pr. Chem. 1901, 63, 49), the best oil of bucco or buchu leaves contains 10 p.c. of hydrocarbons, consisting of a variety of *d*-limonene and dipentene; 60 p.c. of a ketone $C_{10}H_{18}O$, $[\alpha]_D$, −16°6′, b.p. 208·5° – 209·5°, which, on reduction, yields a menthol not identical with the natural product; 20 p.c. of diosphenol; 5 p.c. of resin; and 5 p.c. of other constituents (Kondakoff, J. pr. Chem. 1896, 54, 433). After removing diosphenol from the oil of buchu leaves, Tschugaeff succeeded in obtaining xanthogenide derivatives of *d*-menthol from a fraction of the residue (J. Russ. Phys. Chem. Soc. 1910, 42, 714; Skovortsoff, *ibid.* i. 55). Diosphenol or buchu camphor (Bialobrzeski, *l.c.*; Kondakoff, *l.c.*; Semmler and McKenzie, *l.c.*; Semmler, Chem. Zeit. 1906, 30, 1208; Kondakoff, Chem. Zentr. 1905, ii. 1252; Chem. Zeit. 1908, 1090, 1100) is optically nactive, has m.p. 82°, b.p. 109°–110°/10 mm., 232°/755 mm. Its composition is probably $C_{10}H_{16}O_2$. It is a phenolic aldehyde, yielding an oxime, m.p. 156° (Semmler and McKenzie 125°). With hydrochloric acid it yields thymol and a little carvacrol. With hydriodic acid it yields a hydrocarbon $C_{10}H_{20}$, b.p. 165°–168°/762 mm.; whilst with sodium in alcoholic solution it forms (1) a menthol; (2) a crystalline glycol $C_{10}H_{18}(OH)_2$, m.p., 92°; and (3) an isomeric glycol, b.p. 141·5°–145°/13 mm. With alcoholic potash, a hydroxy acid of the terpene series, m.p. 94°, is obtained. This acid has been synthesised, and is identical with the natural product. The dibromide $C_{10}H_{14}O_2Br_2$ and other derivatives of diosphenol have also been obtained.

BUCKTHORN (*Rhamnus cathartica* [Linn.]). This plant is a native of England; it grows to a height of from 15 to 20 feet; its flowers are greenish coloured, and its berries four-seeded. The juice of these when in an unripe state has the colour of saffron; when ripe and mixed with alum, it forms the sap or bladder-green of the painters (*v.* PIGMENTS); and in a very ripe state the berries afford a purple colour. The bark also yields a fine yellow dye.

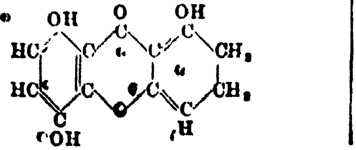
The berries of the *Rhamnus carthartica* (also known as Hungarian berries) have been examined by Tschirch and Polacco (Arch. Pharm. 1900, 238, 409), and evidently contain substances chemically distinct from those which are present in Persian berries.

Ether extracts from an aqueous extract of the berries *rhamnocitrin*, *rhamnolutin*, *rhamnochrysin*, and the residual watery liquid on boiling with dilute sulphuric acid gives, in addition to rhamnocitrin, *β-rhamnocitrin*. The berries already extracted with water contain *rhamnoemodin* and *rhamnonigrin*.

Rhamnocitrin $C_{13}H_{10}O_5$, yellow needles, melts at 221°–222°, and is soluble in alkaline solutions, with a yellow colour. Alcoholic lead acetate gives an organic coloured precipitate, and ferric chloride a green colouration. The solution in sulphuric acid possesses an intense green fluorescence.

Triacetylrhamnocitrin $C_{13}H_7O_5(C_2H_3O)_3$ forms colourless needles, melting at 199°–200°.

Rhamnocitrin appears to be a *dihydrotrihydroxyxanthone*, and probably possesses the following constitution:—



It dyes with iron mordant a green-brown, and with aluminium mordant a bright yellow colour.

Rhamnolutin $C_{15}H_{10}O_6$, small canary-yellow needles, melts above 260°, and gives with lead acetate an orange-red precipitate, with ferric chloride a green-black colouration. Its sulphuric acid solution possesses a strong green fluorescence. *Tetraacetylrhamnolutin* $C_{15}H_6O\ (C_2H_3O)_4$, colourless needles, melts at 182°–183°.

Rhamnolutin dyes aluminium- and iron-mordanted fabrics respectively canary-yellow and green-brown shades. It appears to be a *tetrahydroxyflavone*, isomeric with luteolin and fisetin.

β-Rhamnocitrin $C_{13}H_{10}O_5$ is sparingly soluble in alcohol and acetic acid, but is distinct from rhamnetin ($C_{12}H_{10}O_5$?), and does not contain methoxy- groups. It melts above 260°, and, generally speaking, its reactions are the same as those of rhamnocitrin itself, but, on the other hand, it possesses stronger dyeing property. *Diacetyl-β-rhamnocitrin* $C_{13}H_8O_5(C_2H_3O)_2$ forms colourless needles melting at 190°–191°.

β-Rhamnocitrin, according to Tschirch and Polacco, appears to resemble very closely the β-rhamnetrin of Schutzenberger (*see* PERSIAN BERRIES).

Rhamnoemodin $C_{15}H_{10}O_5$, m.p. 254°–255°, is similar to *frangula emodin* (*R. frangula*) which, according to Oesterle, melts at 250°.

Rhamnonigrin is converted by boiling with nitric acid into *chrysamminic acid*, and by digestion with boiling alcoholic potash into *emodin*.

The **alder buckthorn** (*Rhamnus frangula*) grows naturally, and is very abundant in woods and thickets, in some parts of Britain. The berries of this species are often substituted for those of the above; but they are easily detected, since they contain only two seeds. In a green state they dye wool green and yellow; when ripe, bluish-grey, blue, and green. The bark also dyes yellow, and, with preparation of iron, black (Lawson)

Rock buckthorn (*Rhamnus saxatilis*), yields berries which are used to dye morocco leather yellow. These, in common with the narrow-leaved buckthorn berries (*R. alaternus* [Linn.]) and those of the yellow-berried buckthorn (*R. infectorius* [Linn.]), are sold as Avignon berries. The wood of the *Rhamnus erythroxylon* (which is a native of Siberia, but grows freely in this climate), in a ground state yields the bright-red colour known to dyers under the name of *redwood*.

A. G. P.

BUCK WHEAT (*Fagopyrum esculentum* [Moench.]) is grown mainly for poultry and also for pig- and cow-feeding in Europe. Its flowers furnish excellent pasturage for bees. Kellner gives the analyses on opposite page.

Buckwheat, after soaking in water, furnishes excellent food for cattle and pigs, though not very suitable for young animals.

The globulin of buckwheat has the composition: C 51·69, H 6·90, N 17·44, S 1·16, and O 22·81. It contains about 13 p.c. arginine, 0·6 histidine, 7·9 lysine, and 1 p.c. cystein and a small amount of tryptophan (Johns and Chernoff, J. Biol. Chem. 1918, 34, 439).

The starch of buckwheat occurs in rounded angular grains of small size, showing a distinct hilum and a tendency to agglomerate.

	Water	Protein	Fat	Carbo-hydrates	Fibre	Ash
Seed	14·1	11·3	2·6	54·8	14·4	2·8
Fine meal	14·7	8·6	1·9	72·6	0·8	1·4
Coarse meal	12·0	31·8	8·4	38·3	4·8	4·7
Fine bran	12·0	15·2	4·5	50·0	11·3	7·0
Coarse bran	15·6	8·0	1·8	34·2	37·6	2·8
Husks	13·2	4·6	1·1	35·4	43·5	2·2
Straw	16·0	4·8	1·2	34·6	38·2	5·2
Whole plant, in flower . .	83·7	2·5	0·6	7·8	4·3	1·1
„ „ hay . . .	14·0	10·5	2·1	35·6	31·4	6·4

The flour is largely used in making buckwheat cakes, popular in America, but rarely met with in England. H. I.

BUCURUMANGA RESIN. A fossil resin, occurring in an auriferous alluvium near Bucurumanga, New Granada. It is light-yellow, transparent, somewhat heavier than water, becomes strongly electric by friction; is insoluble in alcohol; swells up in ether, becoming opaque; melts when heated; burns in the air without residue. It resembles amber in outward appearance, but does not give succinic acid on dry distillation. It contains 82·7 p.c. C, 10·8 p.c. H, and 6·50 p.c. O (Boussingault, Ann. Chim. Phys. [3] 6, 507) (*v.* RESINS).

BUFAGIN *v.* BUFOTALIN; and TOAD VENOM.

BUFFALO RUBIN *v.* AZO- COLOURING MATTERS.

BUFOTALIN, the poisonous principle of the toad, $C_{16}H_{24}O_4$, m.p. 148° (decomp.) $[\alpha]_D^{20}$ + 5·4°, is a crystalline neutral substance. Alkali converts it into the unsaturated *bufotalic acid*, proving bufotalin to be a lactone. The other two oxygen atoms are present as alcoholic hydroxyl groups. It dissolves in concentrated sulphuric acid with an orange red colouration which becomes deep red on standing, and shows a green fluorescence. Concentrated hydrogen chloride in the cold eliminates 2 mols of water, forming a pale-yellow crystalline compound *bufotalien* $C_{16}H_{20}O_2$, m.p. 210°. *Acetylbufotalien* separates in lustrous, yellow platelets grouped in rosettes, m p. 184° (decomp.).

Bufotalin is not identical with *bufagin* $C_{18}H_{24}O_4$, obtained from the parotoid gland of the tropical toad *Bufo Agua* by Abel and Macht (J. Pharmacol. and expt. Ther. 1912, 3, 319). This is also dextrorotatory (+11°), sparingly soluble in water, m.p. 217°–218°. (Wieland and Weil, Ber. 1913, 46, 3315).

The Chinese drug 'senso,' prepared from toad skins, appears to contain bufagin, associated with cholesterol, together with adrenaline and *bufotoxin*, a member of the picrotoxin group of poisons (Shimizu, J. Pharm. Expl. Ther. 1916, 8, 347). V. TOAD VENOM.

BUHRSTONE or **BURRSTONE.** A hard, tough rock consisting of chalcedonic silica with a cellular texture, especially suitable for use as millstones for grinding corn, paints, &c. It is white, grey, or creamy in colour. The best stones are from the Tertiary strata of the Paris basin, and have originated by the silicification of fresh-water limestones, the cellular spaces representing the casts of fossil shells and *Chara* seeds. L. J. S.

BUILDING STONE. The essential qualities of a building stone depend on its physical characters rather than on chemical composition. Nevertheless, the broad classification of building stones has a chemical basis, viz.:—

Sandstones and Grits, composed largely of silica in the form of quartz grains.

Limestones and Marbles, consisting of calcium carbonate, sometimes with magnesium carbonate.

Slates, consisting largely of secondary aluminium silicates.

Igneous Rocks (including granite, syenite, diorite, gabbro, porphyry, porphyrite, dolerite, diabase, rhyolite, andesite, basalt) composed of a dense crystalline aggregate of closely interlocking grains of hard silicate minerals, sometimes with quartz.

A few other miscellaneous rocks used as building stones include flint, serpentine, potstone, and laterite. Each of these kinds of rock is considered under its respective heading.

Although a large number of analyses of building stones are on record, these are of little direct value in estimating the quality of a stone. They are, however, useful in indicating whether a limestone is dolomitic (*i.e.* containing magnesia) or clayey in character, and in telling the nature of the cementing material in the case of sandstones. A simple test with acid is often useful in helping to recognise a limestone, otherwise there is usually not much difficulty in allotting different stones to their main classes. Colour and change of colour on weathering are usually connected with the amount and state of the iron present in the stone.

In the decay of building stones in buildings the processes involved are different not only in degree but also in kind from those which take place in the weathering of rocks *in situ*, as considered by geologists. Here chemical action is in general of less importance than that produced by mechanical means, especially by the action of frost and by extreme alternations of temperature, and by the organic action of lichens. The solvent action of pure rain-water is insignificant for all stones except alabaster. Carbonated water has a more pronounced solvent action on limestones and the calcareous cement of sandstones. In the case of silicate rocks[1] the action of carbonated water is extremely slight, unless the felspars have already been previously considerably altered by weathering *in situ*. In towns, however, the action of sulphurous, sulphuric (hydrochloric and nitric) acids brought down by rain-water is of more importance, particularly in the case of limestones. The calcium carbonate is converted into gypsum, and this crystallising with an increase in volume of slightly more than double causes a disruption of the surface layers of the stone. (On the weathering of Portland stone and magnesium limestone in the London atmosphere, *see* E. G. Clayton, Proc. Chem. Soc. 1901, xvii, p. 201; W. Pollard, Summ. of Progress, Geol. Survey United Kingdom, for 1901, 1902, p. 83). Here also the rate of decay is governed more by the state of aggregation of the calcium carbonate than by the chemical composition of the stone; a stone with a cement of mealy calcium carbonate going much more quickly. The sodium and magnesium salts of sea-water blown as spray on buildings often have a deleterious effect. Stones containing nodules of iron-pyrites should be rejected, since this mineral is readily decomposed, giving rise to unsightly stains and producing free sulphuric acid which causes further injury to the stone.

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[1] Here the effect of alternations of temperature is of much more importance owing to the conjunction of minerals possessing different coefficients of expansion. In passing it may also be remarked that igneous rocks (and also jasper) are the only stones used for outside decoration which are capable of retaining a surface polish.

Preservatives against decay include painting the surface with oil-colours; or saturating the surface with a solution of sodium silicate, which may be followed by treatment with a solution of calcium chloride. The carved stonework (limestone) of the Houses of Parliament and the Abbey at Westminster was restored by Sir A. H. Church by the application of baryta water, the crumbly surface layer of gypsum being thereby converted into more resisting barium sulphate.

The different kinds of artificial stone manufactured for building purposes are classified roughly by Howe (*see* references below) as follows:—

1. Stones made of natural rock fragments held together by Portland or magnesium cement. *E.g.* 'Pentuan stone' and concrete.

2. Similar stones subjected to a subsequent hardening process by treating with sodium silicate. Here the action of the cement is modified and hydrated calcium silicates are formed which harden the stone. *E.g.* 'Victoria stone' made from the granite of Groby and Mount Sorrel, Leicestershire, 'Atlas stone,' and 'Hard York non-slip stone' made from sandstone.

3. Stones in which granulated rock or sand is cemented with calcium carbonate. *E.g.* Thom's patent reconstructed stone, many 'lime-sand' blocks, and pumice-, trass-, and pozzolana-lime stones.

4. Stones in which more or less of the calcium carbonate cement is replaced by calcium silicate.

5. Stones cemented by bituminous, asphaltic, or other organic substance.

References.—J. A. Howe, The Geology of Building Stones, London, 1910; J. Watson, British and Foreign Building Stones, Cambridge, 1911; H. Ries, Building Stones and Clay-products, a handbook for architects, New York, 1912; G. P. Merrill, Stones for Building and Decoration, 3rd ed., New York, 1903; J. Hirschwald, Die Prüfung der natürlichen Bausteine auf ihre Wetterbeständigkeit, Berlin, 1908; J. Hirschwald, Handbuch der bautechnischen Gesteinsprüfung, Berlin, 1912; W. A. Parks, Report on the Building and Ornamental Stones of Canada, Dept. Mines, Ottawa, 1912. Reference may also be made to the petrographical text-books of J. J. H. Teall, A. Harker, and F. H. Hatch. L. J. S.

BULBOCAPNINE. *See* under *Corydaline.*

BUNTKUPFERERZ (Ger.). Variegated copper ore. This term is commonly applied, even by English mineralogists, to an ore of copper otherwise known as *Bornite* (*q.v.*), *Erubescite, Phillipsite*, and *Purple Copper Ore.* Called 'horse-flesh ore' by the Cornish miners. L. J. S.

BUPLEUROL. An alcohol found in the higher boiling fractions of the oil of *Bupleurum fruticosum.* Optically inactive, sp.gr. 0·8490/17°, n_D=1·4508; b.p. 209°–210°/762 mm. Has a faint odour of roses. Contains one double linkage and yields an urethane melting at 45°. Probably a dihydro-derivative of nerol of the constitution:

$$(CH_3)_2CH(CH_2)_3{\cdot}C(:CH_2){\cdot}CH_2{\cdot}CH_2OH$$

(Francesconi and Sernagiotto, Atti. R. Accad. dei Lincei, 1913, 22, i. 34, 148; J. Soc. Chem. Ind. 1913, 251).

BURGUNDY PITCH or **NORWAY SPRUCE RESIN.** (*Fichtenharz, Tannenharz*, Ger.; *Poix des Vosges, Poix blanche, Poix jaune, Barras*, Fr.) The resin of *Picea excelsa* (Link.) purified by melting in hot water and straining. It is an opaque, yellowish-brown, hard, brittle resin; its taste is sweet and aromatic. It is very soluble in glacial acetic acid, acetone, and alcohol. Used in making plasters. It is much adulterated. The substance usually sold by this name in England is made by melting colophony with palm-oil or some other fat, and stirring in water to make the mixture opaque (Morel, Pharm. J. [3] 8, 342) (*v.* Resins).

BURNETT'S FLUID. A solution of zinc chloride is commonly known as Sir William Burnett's disinfecting fluid. It is used as a disinfectant and as a preservative of constructional timber.

BURTON WATER CRYSTALS contain, according to Moritz and Hartley, 31·8 CaO, 40·4 SO_3, 1·04 Cl, 5·46 MgO, and 21·19 OH_2 (J. Soc. Chem. Ind. 2, 82).

BUSH SALT. A light-brown or greyish powder prepared by the natives of Ssongea by lixiviating the ashes of the sedge, *Cyperus Haspan*, L. Contains 77·77 p.c. KCl, and 18·48 K_2SO_4, with traces of sodium salts and organic matter (Lenz, Ber. deuts. Pharm. Ges. 1911, 21, 270).

BUSSORAH GUM *v.* Gums.

BUTALANINE *v.* Valine.

BUTANE *v.* Butyl- compounds.

BUTANONE (*Methylethylketone*) *v.* Ketones.

BUTEA FRONDOSA. The *Butea frondosa*, also called *Dhak* or *Pulas*, is a fine tree, 30–40 feet high, belonging to the order *Leguminosæ.* It is common throughout India and Burma, and is found in the North-West Himalaya, as far as the Jhelum River. The flowers, which in the dried condition are known as tísu, késú, kesuda or palás-képpúl, have a bright-orange colour, and, although they are much larger, closely resemble in appearance the common gorse-flower (*Ulex europæus*), with which, indeed, they are botanically allied. Large quantities of the flowers are collected in March and April, and employed by the natives to produce a yellow dye, much used during the 'Holi' festival. The dyeing operation, which consists in steeping the material in a hot or cold decoction of the flowers, is virtually a process of staining, because the colour can be readily washed out. On the other hand, a more permanent result is sometimes produced either by first preparing the cloth with alum and wood ash or by adding these substances to the dye-bath.

From the *Butea frondosa* is also obtained the so-called 'Butea gum' or 'Bengal kino,' employed by the natives for tanning leather, and the tree is of additional interest because in many parts of India the lac insect (*Coccus lacca*) is reared upon it. This latter, as is well known, causes the formation of stick lac, from which shellac and lac dye are prepared.

Butin $C_{15}H_{12}O_5$. The flowers are extracted with water, and the extract digested boiling with a little sulphuric acid. A light viscous precipitate devoid of dyeing property separates, and this is removed while hot and the filtrate left over-night. The clear liquid is now decanted from a small quantity of tarry substance, and partially evaporated on the water-bath. A further quantity of a black viscous precipitate thus separates, and when this has been removed the filtrate, after some days, deposits crystals of the colouring principle. For purification the product is dissolved in a little alcohol, the mixture poured into ether, and the solution well washed with water. The liquid is evaporated, and the residue repeatedly crystallised from dilute alcohol (Perkin and Hummel, Chem. Soc. Trans. 1904, 85, 1459).

Butin crystallises from alcohol in colourless needles with $\frac{1}{2}H_2O$, m p. 224°–226°, and from water in pale-yellow needles with $2H_2O$; dissolves in alkaline solutions with a pale orange-red tint, and gives with alcoholic acetate of lead a faintly yellow almost colourless precipitate. It forms a *triacetyl* derivative $C_{15}H_9O_5(C_2H_3O)_3$, colourless leaflets, m.p. 123°–125°, and a *tribenzoyl* compound $C_{15}H_9O_5(C_7H_5O)_3$, colourless needles, m.p. 155°–157°. On fusion with alkali at 200°–220° butin gives *protocatechuic acid* and *resorcinol.*

When butin is boiled with dilute potassium hydroxide solution, the pale-coloured liquid becomes much darker, and on acidifying an orange crystalline precipitate separates which consists of *butein.*

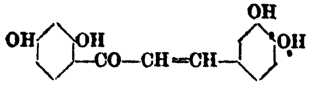
Butein $C_{15}H_{12}O_5,H_2O$, needles, melts at 213°–215°; dissolves in alkaline solutions with a deep orange-red colour, and with alcoholic lead acetate gives a deep-red precipitate. *Acetylbutein* $C_{15}H_8O_5(C_2H_3O)_4$, pale-yellow needles, melts at 129°–131°.

When fused with alkalis butein gives *resorcinol* and *protocatechuic* acid, whereas by the action of boiling 50 p.c. potassium hydroxide solution, *protocatechuic* acid and *resacetophenone* are produced.

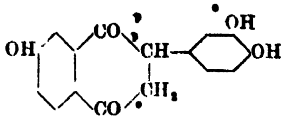
By methylation with methyl iodide butin gives *butin trimethylether* $C_{15}H_9O_2(OCH_3)_3$, colourless plates, m.p. 119°–121°, and also *butein trimethylether* $C_{15}H_9O_2(OCH_3)_3$, yellow leaflets, m.p. 156°–158°. In a similar manner, butein yields not only butein trimethylether, but also butin trimethylether.

The constitution assigned to butein by Perkin and Hummel is that of a *tetrahydroxybenzylidene acetophenone* (*tetrahydroxychalkone*) (1), and to butin that of the corresponding *flavanone* (2):

(1)

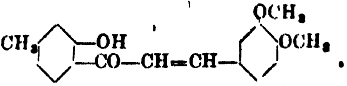


(2)

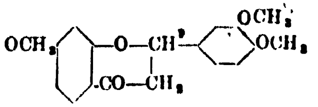


and that these formulæ are correct has been established by the synthesis of butein and butin trimethylethers by these authors. Thus by the condensation of resacetophenone monomethylether with veratric aldehyde, butein trimethylether (I) is produced:

I.



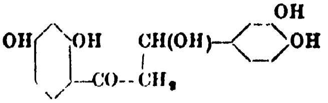
II.



and this, when digested with boiling dilute alcoholic sulphuric acid, a method devised by v Kostanecki and his colleagues (Ber. 1904, 37, 784, 773, 779), gives butin trimethylether (II).

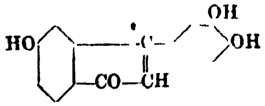
Somewhat later (Ber. 1911, 44, 3502) Göschker and Tambor prepared butein itself by treating protocatechuic aldehyde and resacetophenone in boiling alcohol with potassium hydroxide solution and found this to be identical in all respects with the natural product. *Butein methylether*, yellow needles, m.p. 185°, 3′:4′-*butein dimethylether*, yellow prisms, m.p. 203°, and *butein tetramethylether* (Ber. 1912, 45, 186), colourless needles, m.p. 89°, were also described.

Butein itself is also converted into butin by means of dilute alcoholic sulphuric acid, and the butin can again be transformed into butein by the action of potassium hydroxide solution. With alcoholic potash butin trimethylether also gives butein trimethylether, and these changes are readily explained if it is assumed that the intermediate compound or its trimethyl ether



is the first product of the reaction in each case, and that this subsequently, by loss of water, passes into either chalkone or flavanone, or both.

When butein dissolved in acetic acid is treated with a few drops of sulphuric acid, and the solution is boiled, a new substance gradually separates in the form of crystals, which possess a beetle-green iridescence, and dissolves in alkaline solutions with a deep-blue colour. The acid liquid decanted from the crystals, on dilution with water, gives a brown precipitate soluble in alkalis with a bluish-violet colouration, which dyes mordanted calico shades of a similar character to those yielded by anthragallol. It appears probable that this more soluble substance represents the first product of the reaction, and is subsequently converted into the green iridescent compound. A consideration of the formula of butein renders it unlikely that these new substances are anthraquinone derivatives; on the other hand, it is suspected that by loss of water ring formation takes place, and that an indone derivative of the following type is first produced:—



Butin and butein dye mordanted woollen cloth identical shades, though as butin gives with an alcoholic lead acetate a practically colourless precipitate, it is not to be regarded as a colouring matter. In other words, butin is merely a colouring principle, and is converted during the dyeing operation by the action of the mordant into the colouring matter butein.[1] The following shades are obtained:—

Chromium	*Aluminium*	*Tin*	*Iron*
Reddish-brown	Brick-red	Full yellow	Brownish-black

and these are strikingly similar to those yielded by some of the hydroxybenzylidenecoumaranones artificially prepared by Friedlander and Rüdt (Ber. 1896, 29, 879) (*see* above).

The butea flowers contain but a trace of free butin or butein, and the glucoside present, which has not yet been isolated, is probably that of butin. This glucoside does not decompose readily during the dyeing process, hence the flowers do not dye mordanted cotton. In wool-dyeing, where acid-baths are employed, a better result is obtained, although in this case the shades possess but little strength. If the glucoside is first hydrolysed by boiling the flowers with dilute hydrochloric acid, or if sulphuric acid is employed, and the acid then neutralised with sodium carbonate, on evaporation a material is obtained which readily dyes by the usual methods. Such products give the following shades: with chromium, deep terra-cotta; with aluminium, a bright orange; with tin, bright yellow; and with iron, a brownish-olive. The chromium colour is characteristic, and is much redder in tint than that yielded by any known natural yellow dye. A. G. P.

BUTEA GUM. The juice of *Butea frondosa* (Roxb.), often sent into the market instead of genuine kino. It forms black-brown, slightly lustrous, brittle lumps, has an astringent taste, and yields pyrocatechin by dry distillation. V. Kino.

BUTINENES C_4H_6.

1. *Erythrene*, *vinyl-ethylene* or *pyrrolene*, $CH_2:CH{\cdot}CH:CH_2$, occurs in coal-gas and is said to be formed by passing fusel-oil through a red-hot tube. Obtained by boiling erythrite with strong formic acid or by the action of potassium hydroxide on di-methylpyrrolidine methyliodide. Also by condensing acetaldehyde with ethyl alcohol in presence of alumina or other catalyst. Forms a tetrabromide, m.p. 119°.

2. *Ethyl-acetylene* $CH_3{\cdot}CH_2{\cdot}C{\equiv}CH$. Obtained by treating methyl ethyl ketone with alcoholic potash and phosphorus pentachloride, or by passing acetylene and ethylene through a red-hot tube. Forms a tetrabromide, m.p. 113°.

3. *Crotonylene* $CH_3{\cdot}C{\equiv}C{\cdot}CH_3$. Obtained by acting on butylene bromide or di-bromo-butane with alcoholic potash, or by distilling barium acetate with sulphur. Dilute sulphuric acid converts it into hexa-methyl-benzene.

A butinene is also formed by the destructive distillation of caoutchouc.

BUTTER. Butter is the fatty product prepared from the milk of the cow. When similar substances are obtained from the milk of other mammals, their origin is indicated in the description, *e.g.* goats' butter, buffalo butter. Fatty food substances of vegetable origin and similar to butter in consistency are also sometimes described as butter, but with a prefix, as *vegetable butter, cocoa-nut butter*.

Butter consists of milk- or butter-fat, with water, and small quantities of milk proteins, lactose, mineral salts, and natural colouring matter. The proteins and lactose, together with the mineral matter associated therewith, are spoken of collectively as *curd*. Commercial butter may also contain common salt, preservatives, and colouring matter, added during manufacture. The added salt and preservatives are not included with the curd in giving the composition of butter, but are separately estimated.

Fat exists in milk in the form of minute globules in a state of suspension in the milk serum. In the process of churning, the fat globules coalesce, producing irregularly-shaped granules of butter. These are strained from the serum, or buttermilk, washed with water, and worked into a mass on a table by means of mechanical rollers, or, as in older processes, by hand. Salt, preservatives, colouring matter, are added, if desired, after washing the butter granules with water.

As regards the influence of salt on the changes taking place in storage it has been found that unsalted butter in commercial cold storage keeps as well as, or better than, salted butter. According to Washburn and Dahlberg (Bull. Agric. Intell. 1918, 9, 996), salt, exclusive of its antiseptic property, hastened the deterioration of butter; when stored at −25° (−15° F.), unsalted butter kept as well as salted butter, and the bacteria decreased more rapidly. On the other hand, they, as well as the acidity, increased more rapidly in the unsalted butter at ordinary temperatures.

According to D. C. Dyer (J. Agric. Research, 1916, 6, 927) the unpleasant flavours which develop in butter during cold storage are produced by chemical change in non-fatty ingredients.

Milk may be directly churned for the purpose of obtaining butter, and, in some remote districts, this process is still followed. It is, however, usual to churn *cream*, that is, the fatty layer which rises to the surface on allowing milk to stand or on subjecting it to centrifugal action.

Cream may be churned in a fresh condition before souring has taken place. In such a case, the period of churning is longer, and the operation must be carried out at a lower temperature than when ripened cream or milk is employed. It is therefore usual to churn ripened cream. The ripening may be effected by standing the cream, and is accelerated by the addition of a little buttermilk or pure culture starters containing suitable bacteria. The taste of cream is affected by certain moulds (*Oidium lactic*, and *P. chrysogenum*), and the enzymes secreted by them may develop abnormal flavours in the butter. Mould spores do not germinate or grow in butter.

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[1] This result has been criticised by Göschker and Tambor, who by the employment of mordanted calico obtained from butin very weak shades. It is, however, certain that by the use of mordanted wool a conversion of butin into butein occurs.

Various views are held as to what takes place during the operation of churning. Fleischmann (Book of the Dairy, 159) states that 'the milk-fat is converted from fluid to solid condition by the shaking which it undergoes,' that is, that churning results in the solidification of fat which in milk is in a superfused condition. On the other hand, Richmond's results (Dairy Chemistry, Ap. 339) would indicate that the fat before churning may be in a solid condition. Whether fat as present in milk is surrounded with some form of membrane (Béchamp, Storch) or with a thin watery covering (Fleischmann) the mechanical operation of churning appears to rub away or remove the protective coating, and thus enable the milk globules to coalesce, forming butter. As to the theories regarding the structure of the fat globules in milk, *see* papers by Storch (Analyst, 1897, 22, 197), Beau (Revue Générale du Lait, 2, 15, 1903), and Richmond (Analyst, 1904, 29, 185).

The quantity of water remaining in finished butter is governed by the conditions of manufacture. Churning at too high a temperature renders the removal of excess water during working difficult. It results in over-worked or 'greasy' butter; or butter with an excessive quantity of water. The maximum limit permissible in England for water in butter is 16 p.c. Canada, Queensland, Holland, have the same limit. Victoria has 15 p.c.; Germany, 16 p.c. for salted, and 18 p.c. for unsalted; and Belgium, 16 p.c.

The proportion of curd may vary from 0·2 to 2·0 p.c. according to method of manufacture, lower quantities being present where freshly separated cream is churned than in the case of ripened cream. Well-made butter rarely contains so high a quantity as 2 p.c., and where this quantity is found, examination should be made for the presence of added non-fatty milk solids. The Government Laboratory has found (Jour Board of Agric. 1912, 19, 750) the quantity of curd in imported butter to range from 0·4 to 1·86 p.c., average 1·04. Out of 366 samples only 11 contained more than 1·5 p.c. of curd. Butter taken from factories in Great Britain ranged from 0·34 to 1·86 p.c., in Ireland from 0·53 to 1·87 p.c. No limits have been fixed as to the non-fatty milk solids permissible in butter, but the Butter and Margarine Act, 1907, gives power to the Board of Agriculture and Fisheries to make regulations on the point.

Van Slyke and Hart (J. Amer. Chem. Soc. 1905, 27) state that when 0·5 p.c. or over of lactic acid is in the cream, the casein is present in the butter as casein lactate, but in butter made from sweet cream as calcium casein. They also make suggestions with regard to the relation between casein compounds and mottled butter. Richmond (Analyst, 1906, 31, 178) has found the average amount of casein to be 0·38 p.c., and not to exceed 0·5 p.c.

The mineral matter in butter (to which no foreign substance has been added during manufacture) consists of the inorganic substances derived from the buttermilk enclosed within the butter granules, and from the caseous matter adhering to the fat. It is really the ash of the curd, or the non-fatty milk solids of the butter.

When butter is heated, the fat melts and separates from the aqueous, curdy portion. After allowing this to settle, the fatty layer is filtered through a warm funnel, and the fat obtained as a clear oil, usually of a yellow colour, but under certain conditions almost colourless, setting to a granular crystalline mass. The fat so obtained consists of glycerides of fatty acids together with the natural or added colouring matter, if any, of the butter, and some unsaponifiable substances, *e.g.* cholesterol, associated with the natural fat. The total quantity of the unsaponifiable matter does not exceed 0·4 p.c. (Bömer, Zeitsch. Nahr. Genussm. 1904, 4, 1070).

The glycerides of butter-fat contain butyric, caproic, caprylic, capric, lauric, myristic, palmitic, stearic, and oleic acids, as triglycerides, with, possibly, a small quantity of mono- and diglycerides. Bell has shown the presence of 'mixed' glycerides, and describes (Chemistry of Foods, 45) an oleopalmitobutyrate. Browne (J. Amer. Chem. Soc. 1899, 613) finds 1·0 p.c. of dihydroxystearic acid; but Lewkowitsch throws doubt upon the presence of any hydroxy acids (Oils and Fats, 4th ed. ii. 667). The composition, as given by Bell (Chem. of Foods, 18), is compared with that given by Browne (J. Amer. Chem. Soc. 1899, 21, 807).

100 parts of fat on saponification yield:

	Bell	Browne	
Butyric acid . .	6·13	5·45	
Caproic „ . .	2·09	2·09	2·90
Caprylic „ . .		0·49	
Capric „ . .		0·32	
Lauric „ .		2·57	
Myristic „ . .	19·46	9·89	50·33
Palmitic „ . .		38·61	
Stearic „ . .		1·83	
Oleic „ . .	36·10	32·50	
Dihydroxy stearic acid	-	1·00	

Siegfield (Zeitsch. Nahr. Genussm. 1912, 24, 45) found no stearic acid, and Smedley (Bio. Jour. 1912, 6, 451) found 10 p.c. of stearic acid in butter fat. Holland, Reed and Buckley (J. Agric. Research, 1916, 101; *ibid.* 1918, 719) have also found high proportions of stearic acid present. They found the percentage quantities of various acids in butter-fat as follows: butyric acid, 3·153; caproic acid, 1·360; caprylic acid, 0·975; capric acid, 1·831; lauric acid, [illegible]; myristic acid, 22·618; palmitic acid, 19·229; stearic acid, 11·384; oleic acid, 27·374. These results were obtained by esterification of the butter-fat, and subsequent fractionation of the resulting esters. For details the original paper must be consulted.

Caldwell and Hurtley (Chem. Soc. Trans. 1909, 95, 853) have fractionally distilled samples of butter fat in the vacuum of the cathode light, and determined certain values of the distillates. They conclude that there is no tributyrin in butter-fat, and probably no triolein, the oleic acid being distributed among the glycerides present, most of it as oleostearopalmitin. Caldwell and Hartley (*l.c.*) have also similarly distilled the fatty acids. According to Amberger (Zeitsch. Nahr. Genussm. 1918, 35, 313) butter-fat contains a small quantity (2·4 p.c.) of triolein; the greater part of the oleic acid existing as mixed glycerides. Butyric and other volatile acids are also present as mixed glycerides; tributyrin cannot be isolated. Examination of the alcohol-soluble portion of hydrogenised butter-fat shows that the original fat contains butyrodiolein, butropalmito-olein and oleo-dipalmitin.

The most characteristic feature of butter-fat is the presence of fatty acids soluble in water and volatile in steam; and the earliest work on butter was directed to the estimation, directly or indirectly, of butyric acid, the largest constituent of the soluble or volatile portion.

Hehner and Angell (Butter: its Analysis and Adulterations, Churchill, 2nd ed. 1877), following the suggestion of Chevreul, proposed in 1874 to obtain the butyric acid by distillation of the acids liberated by dilute sulphuric acid after saponification of the fat with alkali. In consequence of the variation in the results, they proposed the determination of the acids insoluble in water, Dupré subsequently adding in the same process the titration of the water-soluble acids (Analyst, 1876). The quantity of insoluble fatty acids is frequently spoken of as the 'Hehner value.' The process consists in saponifying a weighed quantity of the fat with alcoholic potash, liberating the fatty acids from the aqueous, alcohol-free, soap solution with excess of dilute sulphuric acid, filtering and washing with hot water the insoluble acids, finally weighing these, and titrating the dissolved acids. The quantity of soluble acids usually falls between 4·2 and 6·0 p.c. (calculated as butyric acid), and the weight of the insoluble acids between 90 and 87·5 p.c.

Reichert adopted a modification of Chevreul and Hehner's distillation of the butyric acid, operating with a definite quantity of fat under prescribed conditions, and thus avoiding the necessity of the distillation of the whole of the volatile acids. Reichert took 2·5 grams of fat; and the number of cubic centimetres of decinormal alkali required to neutralise the distillate from this quantity, operating as described, was the original Reichert number (Chem. Soc. Trans. 1879, A, 406; Zeitsch. anal. Chem. 1879, 18, 68). Meissl suggested the use of 5 grams of fat (Chem. Soc. 1880, A, 828), and Wollny added a number of modifications (Chem. Soc. 1888, A, 200). This process was adopted by a committee consisting of the Principal of the Government Laboratory and members of the Society of Public Analysts, as the method to be used in the estimation of butter-fat in margarine (Analyst, 1900, 25, 309). The conditions of distillation must be strictly observed, as the whole of the volatile acid is not distilled during the experiment. Richmond (*ibid.* 1895, 20, 218) found only 87 p.c. of the total volatile acids in the distillate. Jensen's results confirm this (Zeitsch. Nahr. Genussm. 1905, 272). Leffmann and Beam used soda dissolved in glycerol for the saponification (Analyst, 1891, 16, 153). The details of the process, as adopted by the committee, are: 5 grams of clear, melted fat are weighed into a flask of a capacity of 300 c.c., and saponified with 2 c.c. of soda (prepared by dissolving sodium hydroxide in equal weight of water), and 10 c.c. of alcohol, by heating on a hot water-bath under reflux condenser for 15 minutes. After evaporation of the alcohol, the dry soap is dissolved in 100 c.c. of hot water, 40 c.c. of normal sulphuric acid and a few fragments of pumice are added, and the flask connected with a condenser. It is then heated so that 110 c.c of distillate are collected in about 30 minutes. The distillate is shaken, 100 c.c. filtered off, and titrated with decinormal alkali, using phenolphthalein as indicator. (Further details as to size of flask, tubes, still-head, condenser, will be found in the Analyst, 1900, 25, 309.) The number of cubic centimetres of decinormal alkali required for neutralisation, when multiplied by 1·1 and corrected to 5 grams, is the 'Reichert-Wollny number.'

The proportion of volatile acids in butter-fat varies. In the late autumn season, in the case of cows fed in the open, the butter-fat contains less butyric acid than it does during the spring and summer. Towards the close of the lactation period, butter fat also shows a depreciation in the amount of volatile acids. Among other factors affecting the character of the fat are the nature of the food, and the sensitiveness of the cows to varying climatic conditions and their surroundings. Hence the uncertainty as regards the limits that should be adopted. In the case of butter made from the milk of mixed herds, when the influence of individual cases does not seriously depreciate the butter from the whole herd, the proportion of volatile acids under ordinary conditions of feeding and housing reaches a maximum in April–May–June, and is at a minimum in October–November. Lewkowitsch has collected a number of results representing the produce of different countries (Oils and Fats, 4th ed. ii. 686). Although the milk from individual cows or small herds may, in consequence of special circumstances, occasionally yield butter fat giving a Reichert-Wollny number below 24, the butter from the mixed milk of herds under normal conditions usually has a Reichert-Wollny number falling between 24 and 32. The Committee on Butter Regulations appointed by the Board of Agriculture in this country recommended that the figure 24, arrived at by the Reichert-Wollny method, should be the limit below which a presumption should be raised that butter is not genuine (Com. on Butter Regns Report, Cd. 1749, 18). France has fixed a minimum limit of 24; Germany, of 25; Sweden, of 23; the United States, of 24; Italy declares butter with a Reichert-Wollny number below 20 adulterated, between 20 and 26 suspicious, above 26 pure; Belgium declares butter to be abnormal, and its sale is prohibited, if the Reichert-Wollny number falls below 28, and if in addition the fat has a Zeiss number above 44 at 40°, a sp.gr. below 0·865 at 100°, a saponification value below 222, and a Hehner number above 88·5.

Sandby Ball (Analyst, 1907, 32, 202) gives results of butters produced in Ireland, and shows that during the months of December and January, when the output of milk is lowest, the Reichert-Wollny number frequently falls below 24. The lowest numbers occur when the milk is derived from cows at the end of the lactation period.

Brownlee (Jour. Dept. Agric. for Ireland, 1910, 10, 438) has published results of analyses of Irish butter produced in 1908-9. He found 16·2 p.c. of samples below 24, 11·4 p.c. below 23, 5·5 p.c. below 22, and 1·4 p.c. below 21. The tables given by Brownlee show that throughout the year the Reichert-Wollny number varies in each case with the percentage output of butter from the particular dairy, and the results confirm the opinion that the chief factor influencing the Reichert-Wollny number is the lactation period of the cows supplying the milk.

The conclusion that butter is genuine because the Reichert-Wollny exceeds 24, may be erroneous, as this number may have been the result of mixing genuine butter having a high Reichert-Wollny number with some other fat. On the other hand, butter falling below 24 may be genuine but abnormal. In order to be in a position to establish the genuineness of butter, the Netherlands Government has organised a system of butter control, by means of which the associated creameries are frequently inspected and the butter produced regularly analysed. Consignments from the factories bear a government label, giving particulars of origin, so that the officials can trace the butter and ascertain the Reichert-Wollny number of the butter produced at the creamery.

Higher homologues of butyric acid volatilised in the steam during the Reichert process do not wholly dissolve in the distillate, and the determination of the insoluble portion affords another index to the character of the fat, as will be seen later.

Butter-fat has a sp.gr. at 37·8°/37·8° of 0·910-0·913 (Thorpe, Chem. Soc. Trans. 1904, 249). The individual data in Bell's results range from 0·9094 to 0·9139, but he states the ordinary range is 0·911 to 0·913. The sp.gr. is affected by prolonged heating of the fat and also by the storage of the fat for a lengthened period

The reading with the Zeiss butyro-refractometer at 45° falls usually between 38 and 42. In 371 samples of genuine butter examined, the range was 37 to 45 (Com. on Butter Regns., Ap. 585). Excluding 14 exceptional butters, the average range was 39·4 to 42·0 (Chem. Soc. Trans. 1904, 249). (Zeiss readings are taken at various temperatures by different observers. To convert the scale divisions observed at a lower temperature into the scale divisions at a higher temperature, deduct 0·55 of a division for each degree of temperature that the reading has been taken below the required temperature; conversely, add 0·55 of a division for each degree of temperature that the reading has been taken above the required temperature).

The saponification value of the fat was suggested by Koëtstorffer (Frdl. 1879, 199), and is frequently known as the Koëtstorffer number. It is the quantity of potash expressed in milligrams required to saponify 1 gram of fat. The glycerides in butter-fat contain acids of comparatively low molecular weights; in consequence, the quantity of potash for saponification will be relatively high when compared with fats in which the glycerides contain only acids of high molecular weight, as in animal fats in general. Butter-fat gives figures on the average between 219·9 and 232·5 (Thorpe). Koëtstorffer gave 227 as a mean figure. This value bears a close relationship to the Reichert number.

The iodine value varies considerably, falling between 26·0 and 35·0 (Hübl), 29·0 and 43·0 (Jensen), and 26·0 and 38·0 (Wollny).

The various data show their dependence upon one another, within certain limits, when a comparison is made. This parallelism is shown in the following table (Thorpe, Chem. Soc. Trans. 1904, 254):—

No. of samples	R. W. number	Specific gravity at 37·8°	Saponification value	Zeiss at 45°	Soluble acids, p.c. on fat	Insoluble acids, p.c. on fat	Mean molecular weight of insoluble acids
7	22·5	0·9101	219·9	42·0	4·3	90·1	266·9
17	23·5	0·9104	221·3	41·5	4·5	89·7	265·5
15	24·5	0·9108	223·3	41·5	4·7	89·4	265·0
27	25·5	0·9110	223·4	41·3	4·8	89·3	264·2
37	26·5	0·9113	225·3	41·0	4·9	88·9	261·9
51	27·5	0·9114	226·7	40·6	5·2	88·7	261·7
78	28·5	0·9118	228·3	40·1	5·4	88·4	260·9
56	29·5	0·9120	229·9	40·1	5·6	88·3	259·6
41	30·5	0·9123	231·4	39·9	5·8	87·9	260·1
18	31·3	0·9125	232·2	39·7	5·7	87·9	258·0
10	32·6	0·9130	232·5	39·4	6·0	87·7	257·8
357							

The examination of butter comprises: (1) the determination of water, fat, curd, salt; (2) examination of the fat; (3) examination of the butter for preservatives, colouring matter, and substances foreign to butter.

1. **Water.** The sample for examination should be not less than 50 grams, and should be placed in a bottle and closed securely with screw-cap or stopper. The bottle is then heated at a temperature of about 50° until the butter-fat has melted, when it is vigorously shaken to emulsify the fat and water. The shaking is continued while the bottle and contents cool, until the butter is of the consistency of thick cream. From 6 to 8 grams are then weighed into a flat-bottomed dish, in which is a glass rod with flattened end. The dish is heated on a steam-bath for an hour with frequent stirring of the butter, after which it is cooled and weighed. It is again heated until the weight is constant. The operation is considerably accelerated by using aluminium dishes, heated on an aluminium hot plate adjusted to a temperature of 100° to 105°.

Patrick (J. Amer. Chem. Soc. 1906, 1613) carries out the estimation of the quantity of water by cautiously heating 10 grams of butter in an aluminium vessel over the direct flame, taking care to avoid over-heating.

In Gray's method (U.S. Dept. of Agric., Bureau of Animal Industry, Circ. 100) 10 grams of butter, weighed on a parchment paper, are placed in a flask together with a little amyl-acetate, and the flask directly heated. The flask is connected with a calibrated tube arranged as a reflux condenser, the condensed water and amyl acetate being collected in a bulb at the bottom of the tube. When all the water is driven off, the tube with the bulb is removed, and inverted, the volume of water being measured in the calibrated portion.

Other methods are Henzold's (in which pumice is mixed with the butter) and Wibel's J. Soc. Chem. Ind. 1893, 630).

Fat. The butter from which the moisture has been expelled is extracted with ether, filtered from curd and salt, and, after evaporation of the solvent, is dried and weighed, or the matter insoluble in ether is weighed, and the fat taken by difference. The fat may also be estimated by the Gottlieb method: 2 grams of butter are washed into a graduated burette tube with about 8 c.c. of warm water, and mixed with 1 c.c. of ammonia (sp.gr. 0·880) and 10 c.c. of alcohol, mixing well after each addition. The tube is cooled, 25 c.c. of methylated ether added, and the liquids mixed; 25 c.c. of light petroleum are then added, and the tube carefully inverted several times to mix the solutions. The volume of the mixed ether solution which separates on standing is measured, and a known portion removed and evaporated.

Shaw (U.S. Dept. of Agric., Bureau of Animal Industry, Circ. 202) takes 25 grams of butter, and using a separator, washes out salt and curd first with hot water, and then with slightly diluted sulphuric acid, finally measuring the volume of fat. The Governments of Queensland, Victoria, and Germany have fixed a minimum limit for fat of 80 p.c.; Italy, of 82 p.c.; and the United States, of 82·5 p.c.

Curd. In the case of butters free from salt and preservative, the curd is the matter not soluble in ether or other solvent. The separate determination of the proteins and lactose must be carried out to decide whether a butter contains added non-fatty milk products. 15–20 grams of butter are weighed in a dish and dried on the water-bath with frequent stirring. The fat is extracted with ether, and the ether-insoluble matter transferred with concentrated sulphuric acid to a Kjeldahl digestion flask, adding the filter paper used for filtration. The quantity of nitrogen multiplied by 6·38 gives the proteins. Richmond gives 6·39 (Analyst, 1908, 33, 180).

The lactose is taken by difference, after deducting from the total curd the proteins and inorganic salts. But it is in all cases preferable to make a direct determination, and this becomes necessary when boric acid is present. The lactose and proteins may then be estimated as follows: The residue from extraction with ether of 20 grams of butter is mixed with about 40 c.c. of water, made just acid with acetic acid, and the proteins precipitated by adding a few drops, being careful to avoid excess, of Fehling's copper sulphate solution. It is then filtered on tared paper, washed, dried at 100°, weighed, and incinerated. The weight less the ash is the proteins. The filtrate is made up to 100 c.c. and an aliquot portion taken for gravimetric lactose determination. Where sugar only is required, the residue from ether extraction may be washed into 100 c.c. flask cleared with copper sulphate, made up to 100 c.c., filtered, and an aliquot portion taken. The quantity of lactose should not exceed 0·4 p.c., and is usually much less.

The matter insoluble in ether contains, in addition to the true curd and other non-fatty solids of milk, common salt, borax, a portion of the boric acid (partly in solution in ether), and certain other preservatives, if these have been added to the butter. The common salt is estimated by extracting the weighed quantity of curd in the total curd determination with hot water, and titrating the solution with standard silver nitrate.

2. Examination of the fat. The examination of the fat to ascertain its purity is one of considerable difficulty, since butter adulteration has been directed to the admixture of fats prepared so as to give no distinctive reaction. All animal fats, such as refined lard and beef fat, and many vegetable fats used for this purpose, have practically no volatile acids. Hence the addition to butter of fats of this class reduces the soluble volatile acids number. Other vegetable fats contain volatile acids only partially soluble in water. To this class belong cocoa-nut oil and palm-kernel oil.

Vegetable fats, unless specially prepared, contain phytosterol, and the detection of this substance establishes the presence of foreign fat. Other fats, as cotton seed and sesamé, give specific reactions, and may therefore be directly tested for. It has, however, been established that the constituent giving the reaction may be communicated to a slight extent to milk and thence to butter through feeding the animals with oil cakes made from these seeds. Positive reactions in these cases must therefore be supported by other evidence. With the object of detecting the addition of foreign fat, it is enacted in some countries that margarine and margarine fats must contain, when prepared for sale, a small quantity of sesame oil, as a tell-tale substance when butter with which such fat has been mixed is examined.

(*a*) The soluble volatile acids are estimated by the Reichert-Wollny process described above.

Reychler (Bull. Soc. chim. 1901, 25, 142) proposed the extension of the Reichert-Wollny process to include the estimation of the volatile insoluble acids. Wauters (Analyst, 1901, 26, 128) modified the Reichert process and made two distillations, determining the values for both soluble and insoluble volatile acids.

Polenske (Zeitsch. Nahr. Genussm. 1904, 273) adopts the Reichert-Wollny process and estimates in the same operation the soluble and insoluble volatile acids. 5 grams of the fat are weighed into a 300 c.c. flask and saponified with 2 c.c. of soda solution and 20 grams of glycerol by heating the flask over the free flame. The flask is cooled below 100°, and 90 c.c. of hot water and a little powdered pumice are added. When the soap is in solution the fatty acids are liberated with 50 c.c. of sulphuric acid (25 c.c. pure H_2SO_4 in one litre), the flask attached at once to a condenser arranged vertically, and heated so that 110 c.c. of distillate are collected in about 20 minutes. The heating is then stopped, and the receiving flask replaced by a measuring jar to catch the drainings of the condenser. The distillate is cooled to 15°, gently shaken, and 100 c.c. filtered off and titrated with decinormal soda. The number of cubic centimetres (multiplied by 1·1 and corrected to 5 grams) is the Reichert-Wollny number.

The remainder of the distillate is poured on the filter paper, and then washed with three quantities, of 15 c.c. each, of water, each of which has been passed in succession through the condenser tube, the measuring jar, and the 110 c.c. flask. These washings are rejected. The 110 c.c. flask is then placed under the filter funnel, and the water-insoluble acids dissolved in alcohol by passing three quantities, of 15 c.c. each, of neutral alcohol, successively through the condenser tube, measuring jar, and filter paper. The alcoholic filtrates are titrated with 1/10 normal soda, using phenolphthaleïn as indicator. The number of cubic centimetres required is the insoluble volatile acids number.

In butter-fat this number varies with the soluble acids number. Polenske (*l.c.*) gave a range of 1·35 insoluble for 20·0 of soluble, to 3·0 insoluble for 30 of soluble. Individual butters may, however, give numbers outside this range. Rideal and Harrison (Analyst, 1906, 31, 254) give results of examination of a number of English butters. Harris (*ibid.* 1906, 31, 353) shows the variation in insoluble acids number for the same soluble acids number. Hesse (Chem. Zentr. 1905, 1, 566) states the limits given by Polenske should be higher. Hesse and Harris (*l.c.*) point out the importance of following exact details of process, particularly in regard to size of pumice. Harris gives varying results obtained by operating with pumice of different sizes. Beerbohm (Milch. Zentr. 1913, 513) states that during lactation, the R.W. number falls but the Polenske number rises.

Cocoa-nut fat gives a soluble acids number by this process of 7–9 and an insoluble acids number of 15–18. Hence the addition of this fat to butter depresses the Reichert-Wollny number, and increases the insoluble volatile acids number. At the same time, the Zeiss and iodine numbers would be lowered, and the saponification value would be increased. Thus, while the Polenske value alone might not itself be sufficient evidence of adulteration in cases of small quantities of admixed cocoa-nut fat, the disturbance of the co-relation between the other numbers would establish the presence of the adulterant. Palm-kernel fat has a Reichert-Wollny number of 5, and insoluble volatile acid number of 10–12; other vegetable and animal fats have a total volatile acids number less than 1. The addition of palm-kernel oil would operate in a similar manner to that of cocoa-nut fat; animal fat would depress both the soluble and insoluble volatile acids, but the former to a greater extent than the latter. Thorp (Analyst, 1906, 31, 173) makes a second distillation in the ordinary Reichert process, after addition of more water, and obtains an increased value for the total insoluble volatile acids. He gives results of examination of butters and mixtures.

Muntz and Coudon (Mon. Sci. 1904, 18; Analyst, 1905, 30, 155) have devised a similar method for determining the ratio between the soluble and insoluble volatile acids. They saponify 10 grams of fat with hot strong aqueous potash, dissolve the soap in water, add phosphoric acid solution, and distil 200 c.c., using a spiral dephlegmator of considerable length. The distillate is filtered, and the soluble acids titrated. The insoluble acids in the condenser tube and flask, and on the paper are also dissolved in alcohol and titrated. They found that pure butters yielded from 4·79 to 6·01 p.c. of soluble volatile acids (as butyric acid) and 0·5 to 0·87 p.c. of insoluble; while cocoa-nut fat gave 1·15 to 1·27 p.c. soluble, and 3·06 to 3·63 p.c. insoluble. They determine the following ratios:

$$\frac{\text{insol. vol.}}{\text{sol. vol.}} \times 100 = 9{\cdot}1\text{–}15{\cdot}6$$

for genuine butter, and 250·3 to 282·3 for cocoa-nut fat.

Vandam (Analyst, 1901, 26, 320) determined the ratio between the total fatty acids soluble in 60 p.c. alcohol, and those soluble in the alcohol but insoluble in water. Robin (Compt. rend. 1906, 143) practically applies the same principle in his method. He found that the ratio $\frac{\text{insol.}}{\text{sol.}} \times 10$ was 8·3 to 12·7 butter, 232 for margarine, and 226 for cocoa-nut fat. Shrewsbury and Knapp (Analyst, 1910, 35, 385) remove the acids soluble in water, and then determine the solubility of the remaining fatty acids in dilute alcohol. They find a solubility figure of 28 for butter and 163 for cocoa-nut fat. It has been shown (Caldwell and Hurtley, Analyst, 1909, 34, 274) that lauric and myristic acids are the chief constituents of cocoa-nut fatty acids, but that these acids are only present to a slight extent in butter; and these processes are therefore based upon the solubility in 60 p.c. alcohol and insolubility in water of these acids. Fendler (Zeitsch. Nahr. Genussm. 1910, 19, 544; Analyst, 1910, 35, 355) has a similar process.

Avé-Lallemant (Zeitsch. Nahr. Genussm. 1907, 14, 317) precipitates the neutralised, alcohol-free soap solution with barium chloride, and determines the baryta values for the soluble barium salts, and for the insoluble barium salts. He finds that normal butter has insoluble baryta value of 247 to 251, and soluble baryta value of 50 to 65. The value [insol. —(200+soluble)] is negative for butter, whereas other fats have a positive value not less than 39. (*See* also Fritzsche, Zeitsch. Nahr. Genussm. 1907, 14, 329.)

Ewers (*ibid.* 1910, 19, 529) proposes a method depending upon the different solubility of the magnesium salts of the fatty acids, and on the varying solubility in petroleum spirit of the fatty acids from the soluble magnesium salts.

Various methods have been proposed to distinguish between cocoa-nut fat and butter fat by means of the solubilities of the silver salts of the distilled acids in the Reichert-Wollny process (K. Jenson, Analyst, 1905, 30, 396; O. Jenson, Zeitsch. Nahr. Genussm. 1905, 10, 265; Kirschner, *ibid.* 1905, 9, 65; Wijsman and Reijst, *ibid.* 1906, 11, 267; Dean, Ann. Chim. anal. 1906, 11, 121). Of these, the method of Kirschner has been much used in this country in connection with the Reichert-Wollny-Polenske process. As it gives a measure of the amount of butyric acid present, and eliminates the reading in the ordinary R.W. process due to the presence of other soluble volatile acids, it is of special value for the detection in butter of margarine mixtures containing coconut or palm-kernel fats. The Kirschner process is carried out as follows: To the 100 c.c. which have been neutralised with baryta for the R.W. No. 0·5 gram of Ag_2SO_4 is added, and after standing for 1 hour with occasional shaking, the liquid is filtered through a dry paper. 100 c.c. are taken; 35 c.c. water, 10 c.c of dilute H_2SO_4 (as in the Polenske method), and a piece of aluminium wire are added; and the distillation carried out as before, 110 c.c. being collected in 20 minutes. 100 c.c. are titrated and the Kirschner number obtained as follows:—

$$K = x \times \frac{121}{100} \times \frac{100+y}{100}$$

(x=titration value of 100 c.c. less blank.)

(y=number of c.c. of baryta solution used in titration of original R.W. No.)

Bolton and Revis (Analyst, 1911 333) and Bolton, Richmond, and Revis (Analyst, 1912, 183) give the results for a number of mixtures, and formulæ and curves for the calculation of the amount of cocoanut or butter-fat present They suggest the following table for the relation between the Kirschner and Polenske numbers:—

Kirschner	Polenske
20	1·60
22	2·10
24	2·65
26	3·20

Cranfield (Analyst, 1915, 441) gives the R.W., Kirschner, and Polenske values for a large number of butters analysed at the Midland Agricultural and Dairy College, showing similar relations between the Kirschner and Polenske figures.

Bolton, Richmond, and Revis point out that if an allowance of ±1 is made in the Polenske value corresponding to any particular Kirschner value, the presence of less than 5 p.c. of cocoanut fat will cause the Polenske value to fall outside the limit, except in cases of special feeding of cows.

Dons (Zeitsch. Nahr. Genussm. 1908, 15, 75) has modified the process. The mixed fatty acids are treated with water to remove the soluble portion. Caprylic acid, which remains behind with the insoluble acids, is removed by distillation, and estimated in the distillate by precipitation with silver nitrate solution. Pure butter-fat gives a value 1·6 to 2·0 and cocoa-nut fat 5·3.

Juckenack and Pasternack (Zeitsch. Nahr. Genussm. 1904, 7, 193) proposed to determine the presence of cocoa-nut oil in butter from the relationship between the Reichert - Wollny number and the saponification value. They point out that according to the formula [R.W. −(sapon. value−200)] butter fluctuates between −3·5 and +4·25. For cocoa-nut oil its value is −47. Harris (Analyst, 1906, 31, 355) has shown that the method of reasoning suggested is of no value for small admixtures of cocoa-nut fat with butter.

[illegible] and Amberger (Zeitsch. Nahr. Genussm. 1909, 17, 23) distil separated solid fatty acids in a current of steam in special flask, and precipitate the cadmium salts in distillate.

Hanuš (*ibid.* 1907, 13, 18) and Hanuš and Štekl (*ibid.* 1908, 15, 577) and Fendler (*ibid.* 1910, 19, 544) propose methods based upon the distillation of the ethyl esters of the fatty acids. Fendler prepares the esters after the manner of Henriques (Analyst, 1898, 23, 181) and collects the esters boiling below 300°. This fraction would include the ethyl esters of the acids up t and including myristic acid. The volume i the case of butter ranges from 2·5 to 6·1; cocoa nut fat, 40 to 42; and lard, 0·5 to 1·1 c.c.

Caldwell and Hurtley (*l.c.*) state that smal quantities of cocoa-nut fat can be detected b the fractional distillation in a high vacuum o the fatty acids.

(*b*) The foregoing tests for the detection o the adulteration of butter-fat are based upon th disturbance of the ratio existing in normal o average butter-fat between the proportions o soluble and insoluble acids. It has, however been shown that special feeding may affect thi relationship and produce butter giving abnorma results. Uncertainty as to the conclusions t be drawn may be removed if direct evidence i obtained from the application of specific tests The following qualitative tests may be applied :—

Phytosterol test for detection of vegetable fat (Bömer, Zeitsch. Nahr. Genussm. 1901, 4, 1070 and 1902, 5, 1018).—The absolute alcoho extract of the unsaponifiable matter from 10 grams of fat is treated with acetic anhydride the excess of which is removed, and the acetate dissolved in alcohol, crystallised, and recrystallised several times. Cholesteryl acetate melts a 113·5° to 114·5°, while the melting-point o Phytosteryl acetate is about 129°. If the melting-point of the mixed acetates from the sampl under examination is between 116° and 117°, i is probably adulterated with vegetable fat; i above 117°, vegetable fat is certainly present The test is not of value if paraffin wax is als present.

Hinks' test for cocoa-nut fat (Analyst, 1907 32, 160).—5 c.c. of the fat are dissolved i 10 c.c. of ether, and the solution cooled in ice After half an hour, it is rapidly filtered, th ether evaporated from the filtrate, and the fatt residue dissolved in 96 p.c. (vol.) alcohol. Th solution is cooled to 5° for 15 minutes, filtered rapidly, and the filtrate cooled to 0°. Th deposit which separates at this temperature i then examined on a cold slide under a powe of about 250. Butter fat yields a deposi of round granular masses; cocoa-nut fat, fin needle-shaped crystals; and mixtures of butte and cocoa-nut fat, fine feathery crystals attache to the granular butter masses. The test i capable of detecting 5 p.c. of cocoa-nut fat i butter fat.

Badouin test for sesamé oil.—5 c.c. of the fa are mixed in a tube with 5 c.c. of HCl (sp.gr 1·19) and 0·1 c.c. of a 2 p.c. furfural solution The mixture is well shaken and allowed to stand The aqueous layer which separates assumes reddish colour in presence of sesamé oil. Butter coloured with some aniline dyes give with hydrochloric acid a pink-to-violet colouration, and i such a case the acid and fat mixture must b heated until colourless before the addition o the furfural solution.

Halphen test for cotton seed oil.—5 c.c. of th fat are dissolved in 5 c.c. of amyl alcohol, 1 c.c of a solution of sulphur in carbon disulphide i added, and the mixture heated for 20 minute at 105° in a brine-bath. A red colouration i produced in presence of cotton-seed oil. Th chromogenetic substance may, however, i exceptional cases, be communicated to butter b feeding cows with cotton cake; and a positiv reaction must be confirmed by other data of the examination.

(c) The specific gravity and the Zeiss reading should be taken and considered in conjunction with and relation to the data for the Reichert-Wollny number, saponification and iodine values.

Of other physical methods there may be mentioned:

Valenta test.—3 c.c. of fat are dissolved in an equal volume of glacial acetic acid, and then allowed to cool while being stirred with a thermometer. Immediately a turbidity is noted, the temperature is read. A modification introduced by Jean is to measure the volume of acid dissolved in the fat at 50°. (For recent investigation of factors affecting the Valenta test, *see* Fryer and Weston, Analyst, 1918, 43, 3.)

Crismer test.—This method is an official one in Belgium. 0·5 c.c. of melted fat and 1 c.c. of absolute alcohol are placed in a tube fitted with cork and thermometer, the bulb of which dips into the liquid. The tube is gently heated inside a larger tube until the liquid becomes homogeneous. It is then allowed to cool, and the temperature noted when turbidity appears. This point is the critical temperature of dissolution (Crismer, Analyst, 1897, 22, 71). Vandam has shown how the alcohol used in the test may be standardised by means of petroleum spirit (Ann. des Falsifications, 1919, 260).

Butter fat gives a result varying from 50·5 to 57, whilst margarine has a value over 65 if it is composed of animal fat, and under 50 if prepared from vegetable fat. The fat must be free from moisture and quite clear, and can generally be so obtained by filtration in a hot-water oven through a dried filter paper. The Crismer values of other fats are as follows: sesamé oil, 67·5; almond oil, 64; cotton seed oil, 61·5; arachis oil, 57·5; olive oil, 56; cacao butter, 47, tallow, 34·5; lard, 76–77; palm oil, 22; cocoanut oil, 15–19·5; palm-kernel oil, 13·5 (Stewart, J. State Med. 1918, 26, 312).

3. **Examination for preservatives.**—(*a*) *Boron compounds.* Boric acid or borax is detected by moistening a strip of turmeric paper (filter paper soaked in an alcoholic solution of curcuma and dried) with a drop of water squeezed from the butter, or with the aqueous layer obtained on melting the butter. The paper is then dried. Free boric acid gives a pink colour changed to green with alkali. For borax a drop of dilute hydrochloric acid must be added to the paper before drying.

The boric acid is estimated by Richmond and Harrison's method (Analyst, 1902, 27, 179) or by washing the butter in a separator with hot water, evaporating the aqueous portion after addition of soda, incinerating, and proceeding as in Thomson's process.

A method suitable for rapid determinations is as follows: 10 grams of butter are shaken in a separator with 20 c.c. of hot water and 10 c.c. of decinormal sulphuric acid. The aqueous layer is run off after a few minutes, and the fat washed twice more with small quantities of hot water. The mineral acid in the combined water extracts is then neutralised, with lacmoid as indicator. 2 grams of mannite are now added, and phenolphthaleïn. Decinormal soda is then added until pink colour is permanent. The quantity of soda used after the solution was neutral to lacmoid indicates the proportion of boric acid present. A control experiment should be carried out with pure butter and indicators.

The Committee on Preservatives in Food recommended that borax or boric acid should be the only preservative allowed in butter, and that the quantity should not exceed 0·5 p.c. calculated as boric acid.

(*b*) *Formalin* is detected by the application of Hehner's test (Richmond, Analyst, 1896, 21, 92). A little milk is added to the aqueous layer from melted butter, and the mixture poured on to the surface of sulphuric acid containing a trace of ferric chloride. In presence of formaldehyde a blue ring appears at the juncture of the aqueous and acid layers.

(*c*) *Fluorides.* Fluorine is detected by evaporating the aqueous portion rendered alkaline from about 30 grams of butter, incinerating, and heating the ash in a platinum crucible with strong sulphuric acid. The crucible is covered with a watch-glass coated with wax through which a mark or design has been scratched with a fine instrument. In presence of fluoride the glass will be etched.

O. and C. W. Hehner (Analyst, 1902, 27, 173) indicate how to remove the boric acid if present before testing for fluoride.

(*d*) *Benzoic acid and benzoates.* 10 grams of butter are heated for some time with alcohol acidified with dilute sulphuric acid. The alcoholic extract, after dilution with water, is extracted with ether in a separator. The ether solution is then shaken with dilute ammonia, and the ammoniacal extract evaporated to dryness in a porcelain dish. The residue is dissolved in water, just acidified with acetic acid to ensure that no free ammonia remains, and a drop of ferric chloride solution added. Benzoic acid gives a buff-coloured precipitate.

(*e*) *Salicylic acid.* A portion of the alcoholic solution prepared for benzoic acid is tested directly with a drop of ferric chloride solution. Salicylic acid gives a violet colour.

(*f*) Richmond (Analyst, 1908, 33, 116) points out that formic acid and glucose are also used as preservative agents.

Colouring matters. The colour of butter prepared without addition of artificial colouring matter, varies according to the food of the cows. The yellow colour is due to the yellow pigments which accompany chlorophyll in all green plants, of which carotin and xanthophyll are the most important. The pigment is not made in the animal body, but is derived entirely from the food; fresh green grass contains most, and gives the highest coloured milk fat. There is a difference in breed, but this is not so important a factor as supposed (Palmer and Eckles, J. Biol. Chem. 1914, 17, 191). (For the detection of carotin in butter, *see* J. Ind. Eng. Chem. 1916, 614.) Winter butter from stall-fed cows is nearly colourless. Colouring matter is frequently added to butter during manufacture. Annatto, turmeric, carrot juice, saffron, marigold, safflower and aniline dyes are among the artificial colours employed. Agitation of the butter fat with hot alcohol will give an indication whether colour has been added. Cornelison (J. Amer. Chem. Soc. 1908, 30, 1478) shakes thoroughly 10 grams of melted fat with 10 to 20 grams of glacial acetic acid at about 35°. The acid layer is drawn off and tested with various reagents for the detection of aniline and vegetable dyes. Leeds (Analyst, 1887, 150) has also proposed a scheme for identification of dye.

Annatto and azo dyes may be rapidly tested for as follows: 5 c.c. of melted fat are placed in each of two test-tubes. To one 5 c.c. of hydrochloric acid are added, and the mixture shaken. Azo- dyes will impart a reddish colour to the acid layer. To the second tube add 5 c.c. of ether, and shake, and then 5 c.c. of 10 p.c. potash solution. Shake and allow to separate. If annatto is present, the alkaline layer will be coloured yellow. To confirm the annatto, the alkaline liquid is withdrawn, evaporated to dryness, and touched with a drop of sulphuric acid. Annatto gives an indigo-blue to violet colouration.

Crampton and Simons (J. Amer. Chem. Soc. 1905, 27, 270) point out the use of palm oil as a colouring substance, and its detection by the Halphen and Liebermann-Storch methods for rosin oil.

The further examination of the butter is concerned with its flavour, appearance, rancidity. As regards rancidity, the quantity of free acid dissolved in alcohol may be ascertained, but this is frequently no guide to or measure of the rancidity, which is best judged by smell and taste.

The definition of 'butter' in the Margarine Act, 1887 (50 & 51 Vict. c. 29) is as follows: 'The word "butter" shall mean the substance usually known as butter, made exclusively from milk or cream, or both, with or without salt or other preservative, and with or without the addition of colouring matter.'

The Butter and Margarine Act, 1907 (7 Edw. 7, c. 21) describes milk-blended butter as 'any mixture produced by mixing or blending butter with milk or cream (other than condensed milk or cream).' By the provisions of this Act milk-blended butter may contain a maximum of 24 p.c. of water.

'Renovated' or 'process' butter is a product mainly of the United States. It is defined by Act of Congress as 'butter which has been subjected to any process by which it is melted, clarified, or refined and made to resemble genuine butter.' Butter which is unsaleable through rancidity, mould growths, or other causes, is melted, and the oil separated from the curd and water. The oil is then aërated by 'blowing' with air, and afterwards emulsified with fresh milk inoculated with a bacterial culture. It is then churned and worked as for ordinary butter.

Crampton (J. Amer. Chem. Soc. 1903, 25, 358) gives details of analyses and tests. Several similar processes have been patented here, and in some factories the melting and purification of inferior butter is now carried on. Hence such products might contain crystalline fat, and the microscopical examination is now of no value as a test for foreign fat.

'Factory' butter is butter which has been reworked or blended with other butter; by 'dairy' butter is understood butter made at the farmer's homestead, whether from whole milk or cream; and the term 'creamery' butter is generally applied to butter made from cream separated by centrifugal force from the mixed milk of a number of herds in premises specially utilised for the purpose (*see* the Report of the Committee of the Department of Agriculture for Ireland, on the Irish Butter Industry, Cd. 5092, 1910).

In hot countries, owing to the rapid decomposition of ordinary butter, the clarified fat, free from water and curd, is prepared for sale, as 'schmelzbutter,' 'ghee.'

Trimen (Analyst, 1913, 242) has described the preparation of 'Samna' or 'Samn,' the Egyptian product corresponding to the 'ghee' of India. Whole milk is churned in goatskins until the butter (zibda) forms. The zibda is collected from the villages by the samna makers, who heat in large pans until it melts, the samna being poured off from the water and curd. Its keeping properties are much superior to those of butter, and it may be used years after it has been made. It is pale yellow in colour, possessing a smell, sometimes cheesy, sometimes acid, frequently rancid, and always unpleasant to European ideas. Both Egyptian samna and Indian ghee are largely made from buffalo milk, and unless artificially coloured are very pale. Syrian samna is generally believed to be made from sheep and goats' milk. Trimen gives the results of analysis of a number of samples. (For other analyses of ghee, *see* Bolton and Revis, Analyst, 1910, 343; *ibid.* 1911, 392; and Kesava Menon, J. Soc. Chem. Ind. 1910, 1428).

G. S.

BUTTERINE *v.* MARGARINE.

BUTTER SUBSTITUTES *v.* MARGARINE.

BUTTER SURROGATE *v.* MARGARINE.

BUTTER, VEGETABLE. A greasy substance expressed from the kernel of the *Bassia butyracea* (Roxb.), a native of North India. This grease is said to make excellent soap. Shea butter is obtained from the *Butyrospermum Parkii*, of West Africa, and has been used in making candles and soap. The butter-tree of Sierra Leone is the *Pentadesma butyracea* (Sabine), the fruit of which yields much grease, and is eaten by the negroes (*v.* OILS and FATS).

BUTTER YELLOW. *Benzeneazodimethyl aniline* $C_6H_5\cdot N:N\cdot C_6H_4\cdot N(CH_3)_2$. A yellow colouring matter (m.p. 115°); insoluble in water, soluble in dilute HCl, with red colour; soluble in fats. Used for colouring butter (Witt. Griess. Ber. 1877, 10, 528) (*v.* AZO- COLOURING MATTERS).

BUTTERS, MINERAL. A term formerly applied to several of the metallic chlorides, *e.g.* chlorides of antimony, tin, bismuth, zinc, &c.

BUTYL. A univalent radical yielding four isomeric mono- derivatives:

(1) $CH_3\cdot CH_2\cdot CH_2\cdot CH_2X$ (normal);
(2) $CH_3\cdot CH_2\cdot CHX\cdot CH_3$ (secondary);
(3) $(CH_3)_2CH\cdot CH_2X$;
(4) $(CH_3)_3CX$ (tertiary).

BUTYL COMPOUNDS.

Butyl alcohol. Tetryl alcohol C_4H_9OH. All the four possible bodies corresponding to this formula are known.

1. *Normal butyl alcohol*: *butanol*; *propyl carbinol* $CH_3\cdot CH_2\cdot CH_2\cdot CH_2OH$; b.p. 117·42° (corr.) (Thorpe and Rodger, Phil. Trans. 1894, 185, ii. 536; Brühl, Annalen, 203, 16); sp.gr. 0° =0·8233, 20°=0·8109, 40°=0·7994, 98·7° = 0·7738, 20°/4°=0·8099 (B.); μ_a = 1·39909, mol. refraction =35·45 (B.). Occurs in the heavy

oil of Cognac brandy to the extent of 49 p.c. Is not formed in the fermentation of sugar produced by elliptical yeast (Claudon and Morin, Chem. Soc. Trans. 1887, ii. 714). Is produced by the action of sodium amalgam upon butyryl chloride and butyric acid (Saytzeff, Zeitsch. Chem. 1870, 108; Linnemann, Annalen, 161, 178). Also by the fermentation of glycerol by *Bacillus butylicus* and certain other bacteria in presence of calcium carbonate and various foodstuffs, *e.g.* ammonium tartrate; the yield amounts to 9 p.c. of the glycerol used. Butyric acid and a little ethyl alcohol are also formed (Fitz, Ber. 9, 1348; Vigna, Ber. 16, 1348). Is also produced by the action of nascent hydrogen (iron and acetic acid) upon crotonaldehyde and trichlorobutyraldehyde (Lieben and Zeisel, Monatsh. 1, 825, 842).

Beyerinck has shown that the *Bacillus butylicus* of Fitz (Ber. 1882, 867) is in reality the butyric ferment. The true butylic ferment, *Granulobacter butylicum*, has been isolated in a pure condition, and an account of the whole fermentation process is given (J. Soc. Chem. Ind. 1894, 167; *ibid.* 969). (*See* also Emmerling, Ber. 1896, 2726; 1897, 451; Buchner and Meisenheimer, Ber. 1908, 1410.)

Properties.—Colourless liquid, soluble in 12 parts of water, from which solution it can be separated by means of calcium chloride. Soluble in concentrated hydrochloric acid; is readily oxidised to butyric acid. Fused zinc chloride abstracts water, and yields β-butylene and smaller amounts of normal butylene (Le Bel and Greene, Amer. Chem. J. 2, 24).

Bromine acting on *n*-butyl alcohol yields, with some difficulty, mono-brombutaldehyde, b.p. 235° (Étard, Compt. rend. 114, 753). The action of aluminium amalgam on the butyl alcohols, producing liquid aluminium alkoxides, has been studied by Tistshenko (Chem. Soc. Abstr. 1899, i. 408).

2. ***Iso-butyl alcohol****, isopropyl carbinol-α-hydroxy β-methylpropane* $(CH_3)_2CH\cdot CH_2OH$, b.p. 108·4° (Linnemann, Annalen, 160, 238), 107·5° at 756 mm., Michael and Zeidler (Annalen, 1912, 393, 81), 107·6° (corr.), Thorpe and Rodger (Phil. Trans. 1894, 185, A, 538); sp.gr. 0·7265 at 106·6°/4° (Schiff, Annalen, 220, 102), 0·8168 at 0° (L.), 0·8069 at 15°/15°, 0·8008 at 25°/25° Perkin (Chem. Soc. Trans. 1884, 468); sp. heat=0·686; molecular rotation=4·936 at 17·7° (P.); molecular refraction=35·41; μ_β=1·4007.

Sp.gr. of aqueous solutions (Duclaux, Ann. Chim. Phys. [5] 13, 91):

Percentage of alcohol (by vol.)	2·5	5	6	10
Sp.gr. of aqueous solution at 15°	0·9950	0·9930	0·9915	0·9875

Occurs in fusel oil from potatoes and beet (Wurtz, Ann. Chim. Phys. [3] 42, 129), and combined with angelic and *iso*butyric acids in Roman oil of chamomile (Köbig, Annalen, 195, 96).

Preparation.—By the action of sodium amalgam and water upon β-chlor*iso*butyl alcohol, which results from the action of hypochlorous acid upon *iso*butylene (Butlerow, Annalen, 144, 24). Is formed in small quantity by the action of elliptical yeast upon sugar or glycerol (Claudon and Morin, Chem. Soc. Trans. 1887, ii. 714) By the reduction of *iso*butyric aldehyd with sodium amalgam (Linnemann and Zotta Annalen, 162, 11).

Properties.—Colourless liquid, soluble i 10·5 parts of water, from which calcium chlorid causes it to separate. Smells like fusel oil Is oxidised by chromic acid into *iso*butyric acid acetic acid, carbon dioxide, acetone, and othe products (Kramer, Ber. 7, 252; Schmitt, *ibid* 8, 1361). Zinc dust yields water and *iso*butylene (Jahn, *ibid.* 13, 989).

Treated with iodine and aluminium, aluminium tri*iso*butoxide $Al(C_4H_9O)_3$ is formed. It i a liquid which may be distilled *in vacuo* (Gladstone and Tribe, Chem. Soc. Trans. 1881, 6).

*Iso*butyl alcohol may be catalyticall oxidised to *iso*butyl aldehyde. The vapour o the alcohol mixed with air, is passed over warm freshly reduced copper spirals and the product collected. A yield of 50 p.c. is obtainable (E Orlow, J. Soc. Chem. Ind. 1908, 957).

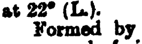
When chlorine is passed into dry *iso*buty alcohol, and the solution subsequently heate gently, the product can be separated into tw fractions, boiling at 80°–100° and 170°–250° The lower fraction consists of *chlorisobutaldehyde*, boiling at 90°–91°; sp.gr. 1·186, 15°/4°. I combines with sodium hydrogen sulphite, an when oxidised with alkaline permanganate yield acetone and hydroxy*iso*butyric acid $C(CH_3)_2OH\cdot COOH$, melting at 78°. A termolecular polymeride $C_{12}H_{21}Cl_3O_3$, which melts at 107°, i obtained by shaking with strong sulphuric aci (A. Brochet, Compt. rend. 114, 1538). If th alcohol is kept cold, the chief product is *dichlorisobutyl oxide* $C(CH_3)_2Cl\cdot CHCl\cdot O\cdot CH_2CH(CH_3)$ boiling at 192·5°/760, and of sp.gr. 1·031, 15°/4° Water is without action on this product at lo temperatures, but at 100° produces hydroge chloride and α-chlor*iso*butaldehyde and di*iso*butylmonochlor*iso*butyral $C(CH_3)_2Cl\cdot CH(OC_4H_9)$ boiling at 218°, and of sp.gr. 0·9355, 15°/4 (A. Brochet, Compt. rend. 118, 1280; *v.* als Brochet, Bull. Soc. chim. 1896, 16; *ibid.* 20).

When chlorine is led into hot *iso*butyl alcohol, chlor*iso*butyric*iso*butyl ester, αβ-dichlor*iso*butyric acid, *iso*butyl ester, mono- and dichlor*iso*butyric aldehyde, *iso*butyric acid, oxy*iso*butyric acid, crotonic acid, CO, CO_2, and methyl chloride are produced. Treating aqueous *iso*butyl alcohol with chlorine water produces *iso*butyric acid, and α-chlor*iso*butyric acid *iso*butyl ester. Chlorine acting on cold dry *iso*butyl alcohol in the light produces 1:2-dichlor*iso*butyl ester (Brochet, Ann. Chim. Phys. [7] 10, 363).

*Iso*butyl alcohol, when acted on by bromine, readily yields *iso*butyl bromide, mixed with *iso*butyl *iso*butyrate, and brom*iso*butaldehyde (Étard, Compt. rend. 114, 753).

(For combinations and derivatives of *iso*butyl alcohol, *v.* Gladstone and Tribe, Chem. Soc. Trans. 1881, 6; Pierre and Puchot, Annalen, 163, 274; and Heindl, Monatsh. 2, 208.)

3. ***Secondary butyl alcohol****, 2-hydroxybutane, methyl ethyl carbinol, butylene hydrate.*



$\begin{matrix}C_2H_5\\CH_3\end{matrix}\!>CHOH$; b.p. 99° at 738·8 mm. (Lieben, Annalen, 150, 114); sp.gr. 0·827 at 0°, 0·810 at 22° (L.).

Formed by the action of water upon the compound of zinc-ethyl and aldehyde:

$$CH_3CH(C_2H_5)O{\cdot}Zn(C_2H_5)$$

thus:

$$CH_3CH(C_2H_5)O{\cdot}ZnC_2H_5 + H_2O = C_4H_9OH + ZnO + C_2H_6$$

(Wagner, Annalen, 181, 261). Also by acting upon secondary butyl iodide with silver acetate and saponifying the resulting acetate by means of potash. Normal butyl alcohol may be changed into the secondary alcohol; the normal iodide is heated with potash, and the normal butylene so obtained on treatment with hydriodic acid yields secondary butyl iodide (Saytzeff, Zeitsch. anal. Chem. 1870, 327). It may also be prepared from the normal isomeride by treating *n*-butylamine with nitrous acid (Meyer, Ber. 10, 130; Kanonnikoff and Saytzeff, Chem. Soc. Trans. 1875, 626).

Properties.—Liquid, with strong odour; upon oxidation yields a ketone $C_2H_5{\cdot}CO{\cdot}CH_3$ (b.p. 80°), and acetic acid (Kanonnikoff and Saytzeff, Chem. Soc. Trans. 1875, 626). Heated with a trace of hydrochloric, hydrobromic, or hydriodic acid, in a sealed tube, to 240°, yields C_4H_8 (pseudo-butylene). It has been separated into its optical antipodes by R. Meth (Ber. 1907, 695); the alcohol has $[\alpha]_D$, 0·32°.

4. *Tertiary butyl alcohol, trimethyl carbinol* $(CH_3)_3C{\cdot}OH$. A solid; m.p. 25·45° (De Forcrand, Compt. rend. 136, 1034); b.p. 82·94° (corr.) (Linnemann, Annalen, 162, 26); 81·5°–82° (Perkin, Chem. Soc. Trans. 1884, 468); 82·25° (Thorpe and Rodger, Phil. Trans. 1894, ii. 539). Sp.gr. 0·7792 at 37° (L.); 0·7788 at 30° (Butlerow, Annalen, 162, 229); 0·7864 at 20°/4°. 0·7802 at 26°/4° (Brühl, Annalen, 203, 17); 0·7836) at 25°/25°, 0·7761 at 35°/35°; molecular rotation at 24·3°=5·122 (P.); μ_β=1·3924, molecular refraction=35·53; crit. temp.=234·9° (Pawlewski, Ber. 16, 2634).

Formed from *iso*butyl iodide by treatment with acetic acid and silver oxide (Linnemann; Butlerow, Annalen, 168, 143); also from *iso*butylamine by treatment with nitrous acid, and from *iso*butyl carbimide $CO{\cdot}N{\cdot}C_4H_9$, by action of potash (Linnemann, Annalen, 162, 12). Can be prepared by allowing 20 grams of tertiary butyl iodide and 50 grams of water to stand in contact for two or three days (Dobbin, Chem. Soc. Trans. 1880, 238).

*Iso*butyl alcohol heated with excess of hydrochloric acid yields a mixture of secondary and tertiary butyl chlorides, and when heated with six volumes of water only the latter is decomposed, yielding the alcohol and hydrochloric acid (Freund, J. Pharm. Chim. [2] 12, 25).

Properties.—Forms rhombic plates or prisms. Unites with water to form a liquid hydrate $2C_4H_{10}O,H_2O$ (b.p. 80°; sp.gr. 0·8276 at 0° (Butlerow, Annalen, 162, 229). On oxidation yields acetone, carbon dioxide acetic acid, and a small quantity of *iso*butyric acid (Butlerow, Zeitsch. Chem. 1871, 485).

The existence of the hydrate $C_4H_{10}O,2H_2O$, m.p. 0°, is confirmed by cryoscopic, density and viscosity determinations (Paternò and Mieli, Atti. R. Accad. Lincei. 1907 (v.), 16, ii. 153).

In sunlight it combines with chlorine, forming tertiary butyl chloride and other substances (D'Otreppe, J. 1881, 512).

Trimethyl carbinol explodes feebly when treated with bromine, yielding *isobutylene bromide* $C(CH_3)_2Br{\cdot}CH_2Br$ boiling at 148° (Étard, Compt. rend. 114, 753).

Tertiary butyl alcohol has a slightly narcotic action when taken internally, and is found in the urine in combination with glycuronic acid (Thierfelder and v. Mering, Chem. Soc. Abstr. 1885, i. 1002).

Nitrohydroxybutanes may be obtained quantitatively as follows: By the action of nitromethane on formaldehyde, in presence of a little potassium carbonate, tertiary nitrotrihydroxybutane $NO_2{\cdot}(CH_2OH)_3$, a white crystalline solid, melting at 158°–159°, is produced. Nitroethane produces tertiary nitrodihydroxybutane $NO_2{\cdot}C(CH_3)(CH_2OH)_2$, melting at 139°–140°. Secondary nitropropane yields nitro*iso*butyl alcohol $NO_2{\cdot}C(Me)_2{\cdot}CH_2OH$, melting at 82° (L. Henry, Compt. rend. 1895, 121, 210).

Butyl bromides. Tetryl bromides C_4H_9Br.

1. *Normal butyl bromide, α-bromobutane*

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br;$$

b.p. 99·9° (corr.) (Linnemann, Annalen, 161, 193); sp.gr. 1·3050 at 0°, 1·2792 at 20°, 1·2571 at 40° (Lieben and Rossi, *ibid.* 158, 161).

Formed from normal butyl alcohol and hydrobromic acid (L. and R. Taboury, Bull. Soc. chim. 1911 [iv.] 9, 124).

By the action of bromine, *αβ*-dibrombutane $C_4H_8Br_2$ (b.p. 166°) is formed (L.).

2. *Isobutyl bromide, α-bromo-β-methyl propane* $(CH_3)_2CH{\cdot}CH_2Br$; b.p. 92·3° (corr.) (Linnemann, Annalen, 162, 34); 91·3° (Perkin, Chem. Soc. Trans. 1884, 459); 91·7° (corr.) (Thorpe); sp.gr. 1·2038 at 16° (L.), 1·2722 at 15°/15°, 1·2598 at 25°/25° (P.). Molecular rotation=8·003 at 16·2° (P.). From *iso*butyl alcohol, bromine, and phosphorus (Wurtz, Annalen, 93, 114). Unites with bromine at 150° to form $C_4H_7Br_3$ (L.). Pure *iso*butyl bromide is an unstable substance, both in the liquid and gaseous states, when heated.

3. *Tertiary butyl bromide, β-bromo-β-methyl propane* $(CH_3)_3CBr$; b.p. 72° at 761·5 mm.; sp.gr. 1·215 at 20°, 1·2020 at 15°/15°, 1·1892 at 25°/25°; molecular rotation=8·238 at 17·8° (P.). Formed when *iso*butyl bromide is heated to 240° (Eltekow, Ber. 8, 1244). Also from trimethyl carbinol and phosphorus pentabromide (Reboul, J. 1881, 409). May also be prepared by leading *iso*butylene into a solution of hydrobromic acid of sp.gr. 1·7 (Roozeboom, Ber. 14, 2396). Is readily decomposed at 300° into *iso*butylene and hydrobromic acid. Water, in the cold, forms the alcohol.

Tribromo tert-butyl alcohol (brometone) $C_4H_7OBr_3$, m.p. 167°–176°, forms white crystals, has a camphor-like taste and odour, is slowly volatile in air, and can be distilled with steam (Aldrich, J. Amer. Chem. Soc. 1911, 33, 386). For pharmacological properties, *see* Houghton and Aldrich, Proc. Amer. Physoil. Soc. 1902).

4. *Secondary butyl bromide, β-brombutane* $CH_3{\cdot}CH_2{\cdot}CHBr{\cdot}CH_3$; b.p. 90°–93° (V. Meyer and Müller, J. pr. Chem. [2] 46, 183); obtained from secondary butyl alcohol by the action of hydrobromic acid, and yields *β* (*γ*)-dibrombutane by warming with iron and bromine.

For observations on the course of the intramolecular transformations of the butyl bromide and chlorides, *see* Michael and Leopold, Annalen, 1911, 379, 263; Michael and Zeidler, Annalen, 1912, 393, 81, Michael, Scharf and Voigt. J. Amer. Chem. Soc. 1916, 38, 653.

Butyl chlorides. Tetryl chlorides C_4H_9Cl.

1. *Normal butyl chloride, a-chlorbutane*

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl$$

b.p. 77·96° (corr.) (Linnemann, Annalen, 61, 197); sp.gr. 0·9074 at 0°, 0·8874 at 20° (Lieben and Rossi, *ibid.* 158, 161); 0·9074 at 0° (L.), 0·8972 at 14°. Formed by the action of chlorine upon *n*-butane (Pelouze and Cahours, J. 1863, 524). More easily by the action of hydrochloric acid upon *n*-butyl alcohol (Lieben and Rossi).

2. *Isobutyl chloride, β-methyl-a-chlorpropane* $(CH_3)_2CH{\cdot}CH_2Cl$; b.p. 68·5° (Linnemann, Annalen, 162, 17); 68·5°–69° (Perkin, Chem. Soc. Trans. 1884, 451); 69·02° (corr.) (Thorpe); sp.gr. 0·8798 at 15° (L.), 0·8953 at 0°, 0·8651 at 27·8°, 0·8281 at 59° (Pierre, Puchot, Annalen, 163, 276), 0·8835 at 15°/15°, 0·8739 at 25°/25° (P.). Molecular rotation at 21·3° = 6·144 (Perkin). Formed by the action of hydrochloric acid or PCl_5 upon the alcohol (Wurtz, *ibid.* 93, 113). By the action of chlorine, hexachlorbutane is produced.

*Iso*butyl chloride is also produced by the interaction of chlorine and *iso*butane in diffused sunlight (Mabery and Hudson, Amer. Chem. J. 19, 245); and also by treating *iso*butylamine cooled to −15° with nitrosyl chloride (Solonina, Chem. Zentr. 1898, ii. 887).

3. *Tertiary butyl chloride, β-methyl-β-chlorpropane* $(CH_3)_3CCl$; b.p. 51°–52° (Perkin, Chem. Soc. Trans. 1884, 451); sp.gr. 0·8658 at 0° (Puchot), 0·8471 at 15°/15°, 0·8368 at 25°/25°; molecular rotation at 15° = 6·257 (Perkin).

Formed (1) by the chlorination of tertiary butane (Butlerow); (2) by the action of iodine monochloride upon *iso*butyl iodide (Linnemann, Annalen, 162, 18); (3) by the action of hydrochloric acid upon *iso*butylene at 100° (Zalessky, Ber. 5, 480; Le Bel, Bull. Soc. chim. 28, 462); (4) by saturating trimethyl carbinol at 0° with HCl gas (Schramm, Monatsh. 9, 619).

Heated with five or six vols. of water to 100°, the alcohol is produced (Butlerow, Annalen, 144, 33). Chlorine in diffused daylight, in the cold, forms $C_4H_8Cl_2$ (b.p. 106°–107°), $C_4H_7Cl_3$ and $C_4H_5Cl_5$, whilst in direct sunlight $C_4H_4Cl_6$ (b.p. in partial vacuum about 115°), and other products are formed (L'Ottreppe, J. 1882, 441).

Tertiary butyl chloride is also formed by the action of PCl_5 on trimethyl carbinol (Janschenko, Chem. Zentr. 1897, ii. 334). It also results, together with *iso*butyl chloride from the action of nitrosyl chloride on tertiary butylamine in xylene solution at −15° *to* −20° (Salonina, *ibid.* 1898, ii. 888).

4. *Secondary butyl chloride, β-chlorobutane* $CH_3{\cdot}CH_2{\cdot}CHCl{\cdot}CH_3$, is produced by the action of nitrosyl chloride on secondary butylamine in xylene solution at −20° (Solonina, Chem. Zentr. 1898, ii. 888).

Butyl cyanates. Only the *iso*-cyanates have been described.

1. *Isobutyl isocyanate. Iso*butyl carbimide $(CH_3)_2CH{\cdot}CH_2{\cdot}NCO$; b.p. 110° obtained by the distillation of *iso*butyl iodide with silver cyanate and sand (Brauner, Ber. 12, 1877).

2. *Tertiary butyl isocyanate*

$$(CH_3)_3C{\cdot}NCO;$$

b.p. 85·5° (corr.); sp.gr. 0·8676 at 0°; remains liquid at −25°. Is formed, together with other substances, when silver cyanate acts upon *iso*butyl iodide (Brauner, Ber. 12, 1874). By the action of hydrochloric acid, forms tertiary butylamine $(CH_3)_3C{\cdot}NH_2$. Potash produces symmetrical di*iso*butyl urea, melting at 242°.

Butyl cyanides. C_4H_9CN.

1. *Normal butyl cyanide, valeronitrile*

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2CN;$$

b.p. 140·4° at 739·3 mm.; sp.gr. 0·8164 at 0° (Lieben and Rossi, Annalen, 158, 171).

2. *Isobutyl cyanide* $(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}CN$; b.p. 126°–128° at 714 mm. (Erlenmeyer and Hell, Annalen, 160, 266); 129·3°–129·5° at 764·3 mm. (R. Schiff, Ber. 19, 567); sp.gr. 0·8227 at 0°, 0·8069 at 20° (Erlenmeyer and Hell); 0·6921 at 129°/4° (S.). Formed by the oxidation of gelatin (Schlieper, Annalen, 59, 15) or casein (Gunckelberger, *ibid.* 64, 76) with chromic acid; also by the action of P_2O_5 upon ammonium *iso*valerate (Dumas, Malaguti, and Leblanc, *ibid.* 64, 334). May be prepared by heating 300 grams *iso*butyl iodide, 98 grams of potassium cyanide, 98 grams of alcohol, and 25 grams of water for three days on the water-bath (Erlenmeyer and Hell).

3. *Tertiary butyl cyanide* $(CH_3)_3C{\cdot}CN$; m.p. 15°–16°; b.p. 105°–106°. Formed by mixing 100 parts of tertiary butyl iodide, 110 parts of mercury potassium cyanide $Hg(CN)_2{\cdot}2KCN$ with 75 parts of dry magnesia, and allowing the mixture to remain for two or three days at a temperature not exceeding 5°. The mass is then treated with water, and distilled on the paraffin-bath (Butlerow, Annalen, 170, 154).

4. *Secondary butyl cyanide*, methylethyl acetonitrile $C_2H_5{\cdot}CH_3{\cdot}CH{\cdot}CN$; b.p. 125°; sp.gr. 0·8061 at 0°. Sodium ($\frac{1}{2}$ eqv.) is dissolved in acetonitrile in benzene, and ethyl iodide (1 eqv.) added (Hanriot and Bouveault, Bull. Soc. chim. (3), 1, 172).

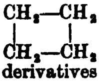
Butyl hydrides. Butanes, tetranes.

1. *Normal butane, diethyl, methylpropane* $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$; b.p. 1° (Butlerow. Zeitsch. Chem. 1867, 363); −0·3°, Burrell and Robertson; sp.gr. 0·60 at 0° (Ronalds, Chem. Soc. Trans. 1865, 54). Critical temp. 153·2; critical press. 35·67 atm. Occurs in crude petroleum (Ronalds, Lefebvre, Zeitsch. Chem. 1869, 185). Formed by heating ethyl iodide with zinc to 150° (Frankland, Annalen, 71, 173; Schöyen, *ibid.* 130, 233). Also by the action of sodium amalgam upon ethyl iodide (Löwig, J. 1860, 397). A colourless gas, insoluble in water. 1 vol. of alcohol at 14·2° and 744·8 mm. absorbs 18·13 vols. of butane (Frankland).

2 *Isobutane, trimethylmethane* $(CH_3)_3CH$. Formed by heating 0·9 part of *iso*butyl iodide with 2·4 parts of aluminium chloride to 120° (Köhnlein, Ber. 16, 562). Also by the action of zinc and water upon tertiary butyl iodide (Butlerow, Annalen, 144, 10). The gas, is readily soluble in alcohol, from which it can be expelled by dilution with water, b.p. −13·4°; critical temp. 133·7; critical press. 36·54 atm. Vapour pressure may be represented by the formula:

$$\log P = -1632{\cdot}661/T + 1{\cdot}75 \log T - 0{\cdot}0158873 + 9{\cdot}06814$$

(Burrell and Robertson, J. Amer. Chem. Soc. 1915, 37, 2482).



C. *Cyclobutane*, tetramethylene, has not yet been obtained, but many derivatives have been prepared by Perkin (Chem. Soc. Trans. 1893, 693; 1894, 950).

Butyl iodides. C_4H_9I.

1. *Normal butyl iodide*

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2I;$$

b.p. 129·8° (corr.) (Linnemann, Annalen, 161, 196); 130·4°–131·4° at 745·4 mm. (Brühl, *ibid.* 203, 21); sp.gr. 1·643 at 0°, 1·6136 at 20° (Lieben and Rossi, *ibid.* 158, 163), 1·6166 at 20°/4° (Brühl). From *n*-butyl alcohol and hydriodic acid (Linnemann, *ibid.* 161, 196). By the action of iodine trichloride at 250° it yields hexachlorethane C_2Cl_6 (Krafft, Ber. 10, 805).

2. *Isobutyl iodide, a-iodo-β-methylpropane* $(CH_3)_2\cdot CH\cdot CH_2I$; b.p. 120·0° (corr.) (Linnemann, Annalen, 160, 240; 192, 69); 83°–83·2° at 250 mm. (Perkin, Chem. Soc. Trans. 1884, 451); 119·94° (Thorpe and Rodger, Phil. Trans. 1894, A, 11, 470); sp.gr. 1·6401 at 0° (L.), 1·6056 at 20°/4° (Brühl, Annalen, 203, 21), 1·6138 at 15°/15°, 1·6007 at 25°/25° (P.). Molecular rotation at 19·4°=12·191 (P.). From *iso*butyl alcohol, phosphorus, and iodine (Wurtz, Annalen, 93, 116).

3. *Secondary butyl iodide, β-iodobutane*

$$C_2H_5\cdot CHI\cdot CH_3;$$

b.p. 117°–118° (Luynes, Bull. Soc. chim. 2, 3); 119°–120° (Lieben, Annalen, 150, 96); sp.gr. 1·6263 at 0°/0°, 1·5952 at 20°/0°, 1·5787 at 30°/0° (Lieben). Formed by distilling erythritol with hydriodic acid (Luynes) or from *n*-butylene and hydriodic acid (Wurtz, Annalen, 152, 23). (See also Clarke, Chem. Zentr. 1908, ii. 1015.)

4. *Tertiary butyl iodide, β-methyl-β-iodopropane* $(CH_3)_3CI$; b.p. 98°–99° (with decom.) (Butlerow); 100·3° (Puchot, Ann. Chim. Phys. [5] 28, 546); sp.gr. 1·571 at 0°, 1·479 at 53° (P.). From tertiary butyl alcohol and hydriodic acid or *iso*butylene and hydriodic acid (Butlerow, Annalen, 144, 5, 22); is easily decomposed (by silver oxide, potash, or by heating with zinc and water), into hydriodic acid and *iso*butylene (Butlerow, Zeitsch. Chem. 1867, 362). Is also decomposed by water in the cold, yielding hydriodic acid and tertiary butyl alcohol. On heating with sodium, yields a mixture of hydrogen, *iso*butylene, and tri*iso*butylene ($C_{12}H_{24}$) (Dobbin, Chem. Soc. Trans. 1880, 236).

Butyl mercaptans $C_4H_9\cdot SH$.

1. *Normal butyl mercaptan*

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot SH;$$

b.p. 97°–98°; sp.gr. 0·858 at 0° (Saytzeff and Grabowsky, Annalen, 171, 251; 175, 351).

2. *Isobutyl mercaptan*

$$(CH_3)_2CH\cdot CH_2SH;$$

b.p. 88°; sp.gr. 0·848 at 11·5° (Humann, Annalen, 95, 256), 0·83573 at 20°/4° (Nasini, Ber. 15, 2882).

3. *Secondary butyl mercaptan*

$$C_2H_5\cdot CH(SH)CH_3;$$

b.p. 84°–85°; sp.gr. 0·8299 at 17°. The mercury compound $(C_4H_9S)_2Hg$ melts at 189° (Reymann, Ber. 7, 1287).

4. *Tertiary butyl mercaptan*

$$(CH_3)_3C\cdot SH$$

is prepared from tertiary butyl iodide, zinc sulphide, and alcohol (Dobbin, Chem. Soc. Trans. 1890, 641). It boils at 65°–67°, and solidifies in a freezing mixture.

Butyl nitrates.

1. *Normal butyl nitrate*

$$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot O\cdot NO_2;$$

boils at 136°; sp.gr. 1·048 at 0° (Bertoni, Gazz. chim. ital. 20, 374).

2. *Isobutyl nitrate* $(CH_3)_2CH\cdot CH_2\cdot O\cdot NO_2$ b.p. 123°; sp.gr. 1·0384 at 0°, molecular rotation at 8·9°=5·18 (P.); molecular refraction=46·72 (P.); b.p. 123·5°–124·5° (Perkin, Chem. Soc. Trans. 1889, 684), sp.gr. 1·0334 at 4°/4°, 1·0264 10°/10°, 1·0124 25°/25° (P.). From silver nitrate, urea, and *iso*butyl iodide (Wurtz, Annalen, 93, 120; Chapman and Smith, Zeitsch. Chem. 1869, 433).

3. *Secondary butyl nitrate* boils at 124°; sp gr. 1·0382 at 0° (Bertoni, Gazz. chim. ital. 20, 375).

Butyl nitrites, nitrobutanes $C_4H_9NO_2$.

1. *Isobutyl nitrite* $(CH_3)_2CH\cdot CH_2\cdot NO_2$; b.p. 67°; sp.gr. 0·89445 at 0° (Chapman and Smith, Zeitsch. Chem. 1869, 433), 0·8878 at 4°/4°, 0·8806 at 10°/10°, 0·8752 at 15°/15°, 0·8702 at 20°/20°, 0·8652 at 25°/25°; molecular rotation at 8·2°=5·51; molecular refraction =43·9 (Perkin, Chem. Soc. Trans. 1889, 686 and 757). Prepared by mixing *iso*butyl alcohol and sulphuric acid, and gradually pouring the cooled mixture, into an aqueous solution of sodium nitrite (1 : 3); the upper layer, consisting of *iso*butyl nitrite, is decanted, washed with potassium carbonate solution, and dried. It is a pale-yellow liquid, is apt to become acid by keeping, when rapid decomposition sets in. Taken medicinally, lowers the blood pressure and produces respiratory paralysis (Dunstan and Woolley, Pharm. J. [3] 19, 487).

2. *Tertiary butyl nitrite* $(CH_3)_3C\cdot NO_2$; b.p. 63°; sp.gr. 0·8914 at 0° (Bertoni, Gazz. chim. ital. 15, 351); 67°–68° (Tscherniak, Annalen, 180, 155). From the alcohol and glyceryl nitrite (B.); also from the iodide and silver nitrite (T.). A yellow, mobile liquid; soluble in alcohol, ether, and chloroform; sparingly soluble in water.

Aromatic nitrobutyl derivatives.

The butyl derivatives of many aromatic nitrohydrocarbons have a musk-like odour, and are sold as 'artificial musk.' '*Musk Baur*, trinitro *meta*butyl toluene $C_6H(CH_3)(NO_2)_3C(CH_3)_3$, is formed by nitrating *meta* butyl toluene with fuming nitric and fuming sulphuric acids. Butyl toluene is formed by Friedel and Craft's method, as described below, by the action of tertiary butyl bromide on toluene in the presence of aluminium chloride. Butyl benzene, ethyl benzene, and xylene are formed at the same time.

An unsymmetrical butyl cresol is formed by adding butyl alcohol and zinc chloride to meta-cresol. When etherified and nitrated, possesses the odour of civet (A. Baur, J. Soc. Chem. Ind. 1892, 307; Dingl. poly. J. 273, 522; J. Soc. Chem. Ind. 1894, 1218).

Butyl xylene may be prepared by passing a current of *iso*butylene gas through a mixture of 5 kilos. *m*-xylene, 50 grams *iso*butyl chloride, and 200 grams aluminium chloride at 10°. The product is washed with water, and the fraction of the oil boiling at 200°–302° collected. Gaseous hydrochloric and hydrobromic acids may be employed to start the reaction (Act. Gesell. für Anilin-Fabriken, Fr. Pat. 372603).

Butyl ethers $(C_4H_9)_2O$.

1. *Normal butyl ether*; b.p. 140·5° at 741·5 mm. (Lieben and Rossi, Annalen, 165, 110); sp.gr. 0·784 at 0°, 0·7685 at 20° (L. and R.), 0·7865 at 0° (Douiner, Annalen, 243, 8). By the action of the sodium derivatives of the alcohol upon *n*-butyl bromide (Reboul, Compt. rend. 108, 39).

2. *Isobutyl ether* $[(CH_3)_2CH{\cdot}CH_2]_2O$; b.p. 122°–122·5° (Reboul, Compt. rend. 108, 162); sp.gr. 0·7616 at 15° (R.). From *iso*butyl bromide and sodium *iso*butylate (R.). The action of *iso*butyl iodide upon potassium *iso*butylate—which, according to Wurtz, yields this ether—really gives a mixture of di*iso*butylene and *iso*butyl alcohol (Reboul).

3. *Secondary butyl ether*

$$[C_2H_5{\cdot}CH(CH_3)]_2O;$$

b.p. 120°–121°; sp.gr. 0·756 at 21° (Kessel, Annalen, 175, 50). From ethylidene chlorhydrin, and zinc ethyl (K.). Formed in mere traces only by the action of secondary butyl bromide upon the sodium derivative of the secondary alcohol (Reboul, Compt. rend. 108, 162). Reboul obtained also the following mixed ethers:—

Secondary butyl *iso*butyl ether; b.p. 121°–122°; sp.gr. 0·7652 at 21°;

Normal butyl *iso*butyl ether; b.p. 131·5°; sp.gr. 0·763 at 15·5;

Normal butyl secondary butyl ether; b.p. 131°; sp.gr. 0·7687 at 15°;

Normal butyl tertiary butyl ether; b.p. 124°, but could not obtain the secondary, tertiary, and the ditertiary ethers (Bull. Soc. chim. [3] 2, 25).

Butyl sulphides.

1. *Normal butyl sulphide*

$$[CH_3(CH_2)_3]_2S;$$

b.p. 182°; sp.gr. 0·8523 at 0° (Saytzeff, Annalen, 171, 253). From butyl iodide and potassium sulphide. Fuming nitric acid yields the sulphone $(C_4H_9)_2SO_2$ (m.p. 43·5°) (Grabowsky, Annalen, 175, 348). Nitric acid of sp.gr. 1·3 converts it into the oxide $(C_4H_9)_2SO$, melting at 32°.

2. *Isobutyl sulphide* $[(CH_3)_2CH{\cdot}CH_2]_2S$; b.p. 172°–173° at 747 mm. (Grabowsky and Saytzeff, Annalen, 171, 254), 170·5° at 752 mm. (Beckmann, J. pr. Chem. [2] 17, 445); sp.gr. 0·8363 at 10° (B.).

Isobutyl disulphide $(C_4H_9)_2S_2$; b.p. 220° (Spring and Legros, Ber. 15, 1940).

3. *Secondary butyl sulphide*

$$(CH_3{\cdot}CH{\cdot}C_2H_5)_2S;$$

b.p. 165°; sp.gr. 0·8317 at 23° (Reymann, Ber. 7, 1288).

Butyl thiocarbimides. Butyl mustard oils; *iso*thiocyanates.

1. *Normal butyl thiocarbimide*

$$(C_4H_9)NCS;$$

b.p. 167° (Hofmann, Ber. 7, 512). From *n*-butylamine, carbon disulphide, and alcohol (H.).

2. *Isobutyl thiocarbimide*

$$(CH_3)_2CH{\cdot}CH_2{\cdot}NCS;$$

b.p. 162°; sp.gr. 0·9638 at 14° (Hofmann, Ber. 7, 511).

3. *Secondary butyl thiocarbimide*

$$C_2H_5{\cdot}CH(CH_3)NCS;$$

b.p. 159·5°; sp.gr. 0·944 at 12°. Occurs in the ethereal oil from spoonwort (*Cochlearia officinalis*) (Hofmann, Ber. 2, 102; 7, 512).

4. *Tertiary butyl thiocarbimide*

$$(CH_3)_3C{\cdot}NCS;$$

m.p. 10·5°; b.p. 140° at 770·3 mm.; sp.gr. 0·9187 at 10°, 0·9003 at 34° (Rudnew, Bull. Soc. chim. 1880, 300). Has a pleasant aromatic odour.

BUTYLAMINES.

1. **Monobutylamines.**

(*a*) *Normal butylamine, aminobutane*

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2;$$

b.p. 75·5° at 740 mm. (Lieben and Rossi, Annalen, 158, 172); sp.gr. 0·7553 at 0°, 0·7333 at 26° (L. and R.), 0·7401 at 20° (Linnemann and Zotta, Annalen, 162, 3). Formed by the action of potassium hydroxide upon butyl cyanate (Lieben and Rossi); also from propyl cyanide by zinc and sulphuric acid (Linnemann and Zotta, Annalen, 162, 3), or from nitrobutane by action of tin and hydrochloric acid (Züblin, Ber. 10, 2083). Is miscible with water; reduces copper, silver, and mercury solutions in presence of alkalis. The chloride forms a yellow crystalline compound with $PtCl_4$, which is almost insoluble in cold water.

(*b*) *Isobutylamine, a-amino-β-methylpropane* $(CH_3)_2CH{\cdot}CH_2{\cdot}NH_2$; b.p. 68° (Schiff, Ber. 19, 565), 68°–69° (Perkin, Chem. Soc. Trans. 55, 694); sp.gr. 0·7357 at 55° (Linnemann, Annalen, 162, 23), 0·7464 at 4°/4°, 0·7408 at 10°/10°, 0·7363 at 15°/15°, 0·7283 at 25°/25°; mol. rot. at 15·3° 5 692; heat of combustion 726,000. From *iso*butyl cyanate and potash (Linnemann, Annalen, 162, 23); also from *iso*butyl iodide and ammonia (Hughes and Romer, Ber. 7, 511); also from *iso*butyl chloride and ammonia dissolved in water or *iso*butyl alcohol. All three *iso*butylamines are produced, the tri*iso*butylamine in largest quantity. The bases can then be separated by means of ethyl oxalate. The product is first separated into two fractions, the one rich in the mono*iso*butylamine, the other rich in the di- and tri- compounds. To the former water and then ethyl oxalate are added; the primary base is thus converted into the oxamide $C_2O_2(NHC_4H_9)_2$, which is almost insoluble in boiling water, the secondary amine being changed into the ethyl oxamate $C_2H_5O{\cdot}C_2O_2{\cdot}N(C_4H_9)_2$. The other fraction (anhydrous) being poured into ethyl oxalate, the primary and secondary bases are converted into oxamates. The tertiary base is distilled off, and the oxamates are saponified by heating with slaked lime. The calcium oxamates can be separated by crystallisation, the di*iso*butyloxamate being the more soluble in alcohol, from which it separates in slender silky needles (Malbot, Compt. rend. 104, 228).

Can be produced by heating *iso*butyl alcohol with ammoniacal zinc chloride to 260° (Merz and Gasiorowski, Ber. 17, 624), or by the action of caustic potash (10 p.c. solution) upon a mixture of bromine and *iso*valeramide (equal molecules) at 60° (Hofmann, Ber. 15, 769).

Mixed with water, contraction and development of heat are produced. A mixture of equal volumes of water and *iso*butylamine has a sp.gr. of 0·9002 at 15°/15°, instead of the calc. density

0·8081 (Perkin, Chem. Soc. Trans. 1889, 696). With absolute alcohol and the amine similar results were obtained, the sp.gr. of a mixture of equal volumes being 0·791 at 15°/15°, instead of 0·7652, the calculated number.

(*c*) *Secondary butylamine*

$C_2H_5·CH(NH_2)·CH_3$;

b.p. 63°; sp.gr. 0·718 at 23° (Menschutkin, Chem. Zentr. 1898, i. 702). Formed by the action of potash upon secondary butyl cyanate, or of ammonia upon secondary butyl iodide (Hofmann, Ber. 7, 513). Also by the action of dilute sulphuric acid upon secondary butyl mustard oil (Reymann, Ber. 7, 1289).

By the reduction of methyl ethyl ketoxime by hydrogen and finely divided nickel at 160°–170°, secondary butylamine and disecondary butylamine are produced. They are liquids, the latter boiling at 132°/758 mm. and forming an oxalate melting at 104° (Mailhe, Compt. rend. 1905, 113).

Secondary butylamine has been separated into its optical antipodes by Thomé (Ber. 1903, 582); $[\alpha]_D$ 7·42° at 20°.

(*d*) *Tertiary butylamine* $(CH_3)_3C·NH_2$; b.p. 45·2° at 760 mm. (Rudnew, Chem. Soc. Abstr. 1879, 40, 141); 43·8° at 760 mm.; sp.gr. 0·7137 at 3°, 0·7054 at 8°, 0·6931 at 15° (R.). Formed in small quantity by the action of potash upon *iso*butyl cyanate (Linnemann, Annalen, 162, 19; Hofmann, Ber. 7, 513). Also as a by-product in preparing trimethyl acetic acid from trimethyl carbinol iodide and mercuric cyanide (Rudnew).

2. **Dibutylamines.**

(*a*) *Di-normal butylamine*

$(CH_3·CH_2·CH_2·CH_2)_2NH$;

b.p. 160°. Formed in small quantities by the action of potash upon butyl cyanate (Lieben and Rossi, Annalen, 158, 175); also by the action of butyl chloride on ammonia (Berg, Ann. Chim. Phys. [7], 3, 294). Gives $[(C_4H_9)_2NH·HCl]_2PtCl_4$; yellow needles, almost insoluble in cold water.

(*b*) *Di-iso-butylamine*

$[(CH_3)_2CH·CH_2]_2NH$;

b.p. 135°–137°; sp.gr. 0·7577 at 4°/4°, 0·7491 at 15°/15°, 0·7425 at 25°/25° (Perkin, Chem. Soc. Trans. 1889, 697). From *iso*butyl bromide and alcoholic ammonia at 150° (Ladenburg, Ber. 12, 949); also from *iso*butyl alcohol and ammoniacal zinc chloride at 270° (Merz and Gasiorowski, Ber. 17, 627). The hydrochloride $(C_4H_9)_2NH·HCl$ forms plates or leaflets easily soluble in alcohol and water, slightly in ether. The platinum compound forms dark-red prisms, soluble in water, alcohol, and ether (Malbot, Compt. rend. 104, 366). The nitroso- derivative $(C_4H_9)_2N·NO$ is a disagreeably smelling oil; m.p. 0°; b.p. 213°–216° (with decomposition); obtained by the action of potassium nitrite upon the hydrochloride (Ladenburg, Ber. 12, 949).

(*c*) *Di-tertiary butylamine*

$[(CH_3)_3C]_2NH$;

produced as iodide when tertiary butyl iodide and tertiary butylamine are heated to 50°; at 70° the mixture is decomposed, forming isobutylene and tertiary butylammonium iodide (Rudnew). The iodide is easily soluble in water or alcohol; on heating the aqueous solution evolves tertiary butylamine.

3. **Tributylamines.**

(*a*) *Tri-normal butylamine* $(C_4H_9)_3N$; b.p. 211°–215° at 740 mm.; sp.gr. 0·791 at 0°, 0·7782 at 20°, 0·7677 at 40°. From butyl cyanate and potash, together with the mono- and di- compounds (Lieben and Rossi, Annalen, 165, 115). With butyl iodide forms iodide of tetrabutylammonium $N(C_4H_9)_4I$, which crystallises in small plates (L. and R.). Also by the action of ammonia on butylchloride; b.p. 216·5° (Berg, Ann. Chim. Phys. [7] 3, 299).

(*b*) *Tri-iso-butylamine* $(C_4H_9)_3N$; b.p. 177°–180° (Reimer, Ber. 3, 757); 184°–186° (Sachtleben, Ber. 11, 733). Sp.gr. 0·785 at 21° (S.). From di*iso*butylamine and *iso*butyl bromide (R.) From the alcohol and ammoniacal zinc chloride at 270° (Merz and Gasiorowski, Ber. 17, 627); also from *iso*butyl iodide and aqueous ammonia at 160° (Malbot, Compt. rend. 105, 574). Is not miscible with water. Forms salts with hydrochloric, nitric, and sulphuric acids, which are extremely soluble and crystallise with difficulty. The platinum double salt forms large ruby-red crystals (Malbot, Compt. rend. 104, 366).

Butylenes C_4H_8. Three isomeric butylenes are possible and all are known.

1. *Normal* (*a*)-*butylene. Ethyl ethylene* $CH_3·CH_2·CH:CH_2$; b.p. −5°.

Formation.—From normal butyl iodide and alcoholic potash (Saytzeff, J. pr. Chem. [2] 3, 88; Grabowsky and Saytzeff, Annalen, 179, 330). From bromethylene and zinc-ethyl (Wurtz, Annalen, 152, 21), together with butyl alcohol. From normal butylamine and nitrous acid (V. Meyer, Ber. 10, 136). Prepared by digesting on the water-bath 100 grams normal butyl iodide, 200 grams potash, and 150 grams alcohol (90 p.c.) (S.). A gas at ordinary temperatures, which combines readily with hydriodic acid to form secondary butyl iodide; and with hypochlorous acid to form chloromethylethyl carbinol $CH_3·CH_2·CH(OH)·CH_2Cl$. Passed over copper heated to redness forms butadiene $CH_2:CH·CH:CH_2$, which may be polymerised to rubber by means of metallic sodium (Eng. Pat 9722, 1911).

2. *β-Butylene. Symmetrical dimethylethylene* $CH_3·CH:CH·CH_3$; b.p. 1° at 741·4 mm. (Lieben, Annalen, 150, 108): sp.gr. 0·635 at −13·5 (Puchot, Bull. Soc. chim. 30, 188).

Formed by the action of potash upon secondary butyl iodide (Luynes, Annalen, 129, 200; Lieben, *ibid.* 150, 108). Together with *iso*butylene by dropping *iso*- or normal butyl alcohol upon strongly heated zinc chloride (Nevole, Bull. Soc. chim. 24, 122; Le Bel and Greene, Amer. Chem. J. 2, 23). From trithioaldehyde $(C_2H_4S)_3$ and copper (Eltekow, Ber. 10, 1904). By heating a mixture of methyl iodide and allyl iodide with sodium (Wurtz, Annalen, 144, 235).

Preparation.—*Iso*butyl alcohol is allowed to drop upon heated zinc chloride, and the evolved gas is led into sulphuric acid diluted with half its volume of water; this retains the *iso*butylene. The unabsorbed gas is led into bromine, and is again liberated by action of sodium (Le Bel and Greene, Bull. Soc. chim. 29, 306). Two stereoisomeric modifications are known (Wislicenus Chem. Zentr. 1897, ii. 267).

β-Butylene combines with bromine to form a dibromide boiling at 156°–158°. This compound, by the action of potash, forms mono-bromo-pseudo-butylene $CH_3\cdot CBr:CH\cdot CH_3$; b.p. 87°–88° (Hölz, Annalen, 250, 230). Chlorine forms a dichloride; b.p. 112°–114° (Chechoukow, Bull. Soc. chim. 43, 127).

3. *γ-Butylene.* *Iso*butylene, *unsymmetrical dimethyl ethylene* $(CH_3)_2C:CH_2$; b.p. −6° (Butlerow, Zeitsch. Chem. 1870, 236). Liquefied by a pressure of 2–2½ atmospheres at 15°–18°. Is produced by the dry distillation of fats (Faraday, Phil. Trans. 1825, 440); by heating the vapour of fusel oil to redness (Wurtz, Annalen, 104, 249), together with ethylene and ethane; also from light petroleum, 'ligroin' (b.p. 60°–90°) (Prunier, J. 1873, 347); from *iso-* or tertiary-butyl iodide and alcoholic potash (Butlerow, Annalen, 144, 19); by heating trimethyl carbinol and dilute sulphuric acid (1 vol. H_2SO_4 to 2 vols. water) (Butlerow); from *iso*butyl alcohol and zinc chloride, though in very small quantity (Nevole, Bull. Soc. chim. 24, 122).

Preparation.—(1) 5 parts of *iso*butyl alcohol, 5 parts sulphuric acid, 1 part of water and sand are heated together (Lermontow, Annalen, 196, 117). (2) Puchot's method (Ann. Chim. Phys. [5] 28, 508) of heating *iso*butyl alcohol with a mixture of sulphuric acid, potassium sulphate, and gypsum, gives a mixture of pseudo- and *iso*-butylene. (3) A mixture of 2 parts of caustic potash and 3 parts of alcohol (90 p.c.) is slowly added to 2 parts of *iso*butyl iodide, and gently warmed (Butlerow, Zeitsch. f. chem. 1870, 238). Butylene is a gas, with unpleasant smell, slightly soluble in water; combines with hydriodic acid to form tertiary butyl iodide. A mixture of three parts of sulphuric acid and 1 part of water completely absorbs the gas; on distilling the diluted solution trimethyl carbinol is evolved. It forms a mercury compound $C_4H_8(HgNO_3)(Hg_2NO_3)$ (Denigès, Compt. rend. 126, 1043). Oxidising agents—*e.g.* potassium permanganate—form carbon dioxide, formic and acetic acids, and oxalic acid (and in the case of chromium trioxide, acetone) (Zeidler, Annalen. 197, 251). By the action of a mixture of 5 parts sulphuric acid and 1 part of water forms dodecylene (tri*iso*butylene) $C_{12}H_{24}$; b.p. 177·5°–178·5°; sp.gr. 0·774 at 0° (Butlerow, Ber. 6, 561).

Butylene alcohol *v.* ***Butylene glycols.***

Butylene dibromides.

1. *Normal butylene dibromide, αβ-dibrombutane* $CH_3\cdot CH_2\cdot CHBr\cdot CH_2Br$; b.p. 165·6°–166°; sp.gr. 1·876 at 0° (Wurtz, Annalen, 152, 23), 1·8503 at 0°, 1·8204 at 20°/0° (Grabowsky and Saytzeff, Annalen, 179, 332). Formed from α-butylene and bromine (Wurtz); from normal buty bromide and bromine at 150° (Linnemann, Annalen 161, 199). Gives α-butylene by action of sodium.

2. *β-Butylene dibromide, βγ-dibrombutane* $CH_3\cdot CHBr\cdot CHBr\cdot CH_3$; b.p. 158°; sp.gr. 1·821 at 0°. Formed from β-butylene and bromine (Wurtz, Annalen, 144, 236), or by heating α- or β-brombutane with iron and bromine (V. Meyer and Muller, J. pr. Chem. [2] 46, 180). Decomposed by heating to 140° with water and lead oxide, forming lead bromide and methyl ethyl ketone (Eltekow, Chem. Soc. Abstr. 1879, 34).

3. *Iso-butylene di-bromide, αβ-dibrom-β-methyl propane* $(CH_3)_2CBr\cdot CH_2Br$; b.p. 148°–149° at 737 mm.; sp.gr 1·798 at 14° (Linnemann, Annalen, 162, 30), b.p. 149·6° (corr.) (Thorpe), sp.gr. 1·7434 15°/15° (Perkin). From *iso*-butylene and bromine (L.; also Wurtz, Annalen, 104, 249; Hell and Rothberg, Ber. 22, 1737). By heating with water to 150° *iso*-butyraldehyde and *iso*butylene glycol are formed.

4. *Tetramethylenedibromide, αδ-dibrombutane*, $CH_2Br\cdot CH_2\cdot CH_2\cdot CH_2\cdot Br$; boils at 188°–190° (Gustavson and Demjanoff, J. pr. Chem. [2] 39, 543). (*See* also Hainsocourt, Compt. rend. 132, 345.)

5. *ββ-Dibrombutane* $CH_3\cdot CBr_2\cdot CH_2\cdot CH_3$; boils at 144°–145° (Wislicenus and Holz, Annalen, 250, 232).

6. *αγ-Dibrombutane*

$CH_2Br\cdot CH_2\cdot CH_2Br\cdot CH_3$;

boils at 174°–175° (Perkin, Chem. Soc. Trans. 1894, 963).

Butylene cyanide.

Isobutylene dicyanide (*dimethyl succinonitrile*) $CN\cdot C(CH_3)_2\cdot CH_2\cdot CN$; b.p. 218°–220°. By treating an aqueous alcoholic solution of potassium cyanide with γ-butylene bromide, and allowing the mixture to stand for a fortnight. A colourless oil, moderately soluble in water. Heated to 150° with strong hydrochloric acid, it is decomposed into ammonia and dimethylsuccinic acid (Hell and Rothberg, Ber. 22, 1737).

Butylene glycolchlorhydrin, β-chloroisobutyl-alcohol $(CH_3)_2\cdot CCl\cdot CH_2OH$; b.p. 137. From *iso*butylene and hypochlorous acid (Butlerow, Annalen, 144, 25). Soluble in large excess of water. See also Michael and Leighton (Ber. 1906, 2157).

β-Chloro*iso*butyl alcohol is also formed by the union of hydrogen chloride with *iso*butylene oxide, which results from the action of dry powdered potassium hydroxide on chlorotrimethyl carbinol. The last may be prepared from magnesium methyl bromide, chloroacetone and ethyl chloroacetate. β-chloro*iso*butyl alcohol boils at 132°–133°. It forms a nitrate by the action of concentrated sulphuric and nitric acids $C(Me)_2Cl\cdot CH_2NO_3$, and a nitrite $C(Me)_2Cl\cdot CH_2NO_2$ with nitrous acid, which distinguishes it from the isomeric chlorotrimethyl carbinol (L. Henry, Compt. rend. 1906, 142, 493).

Butylene diamines.

1. *Tetramethylenediamine* (*putrescine*), *αδ*-diaminobutane $NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2$, occurs in urine and fæces in cases of cystinuria, and also arises during the putrefaction of herrings. It is prepared by reducing an alcoholic solution of dicyanoethylene with sodium (Ladenburg, Ber. 1886, 780; Lellmann and Winthaer, Annalen, 228, 229); or in a similar manner from succinaldehyde dioxime (Ciamician and Zanetti, Ber. 1889, 22, 1968, 1970). Colourless crystals melting at 27°–28° (C. Z.) and boiling at 158°–160°. Smells like piperidine. It is strongly basic, readily absorbs CO_2, and forms a well-defined dihydrochloride, aurichloride, and platinichloride. The picrolonate is of some physiological importance (Otori, Chem. Soc. Abstr. 1905, ii. 126).

Willstätter and Heubner have prepared the tetramethyl derivative of tetramethylene diamine, and the biquaternary hexamethylammonium salt corresponding to it (Ber. 1907, 3871, 3874). The identity of *aδ*-diaminobutane with putrescine rests on the experiments of Udranszky and Baumann (Ber. 1888, 2938). Brieger (Chem. Zentr. 1907, i. 1703) considers the identity not proven, as also do Willstätter and Heubner (*l.c.*).

2. *Dimethylethylenediamine, βγ-diaminobutane* $CH_3·CHNH_2·CHNH_2·CH_3$, has been prepared by Angeli (Ber. 1890, 1358).

Iso-**Butylacetic acid** *v.* CAPROIC ACID.

Butyl chloral *v.* CHLORAL.

Butyl-lactinic acid *v.* HYDROXYBUTYRIC ACIDS.

Butylene glycols.

1. *Normal-(α)-butylene glycol, aβ-dihydroxybutane* $CH_3·CH_2·CHOH·CH_2OH$; b.p. 191°–192° at 747·1 mm.; sp.gr. 1·0189 at 0°/0°, 1·0059 at 17·5/0°. From normal butylene dibromide (Saytzeff and Grabowsky, Annalen, 179, 332).

2. *β-Butylene glycol, aγ-dihydroxybutane* $CH_3·CH(OH)·CH_2·CH_2OH$; b.p. 203·5°–204° (Kekulé, Annalen, 162, 310); sp.gr. 1·0259 (Wurtz, J. 1873, 474; Bull. Soc. chim. 41, 362). Produced in small quantity by the reduction of dilute aqueous solution of aldehyde by sodium-amalgam (K.). Prepared from *β*-oxybutyric aldehyde by reduction with sodium amalgam (W.).

3. *Isobutylene glycol, aβ-dihydroxy-a-methylpropane* $(CH_3)_2C(OH)·CH_2OH$; b.p. 176°–178°; sp.gr. 1·0129 at 0°, 1·003 at 20°. Produced by the fermentation of sugar in presence of tartaric acid (Henninger and Sanson, Compt. rend. 106, 208). Formed by heating *iso*butylene bromide with potassium carbonate and water (Nevole, Bull. Soc. chim. 27, 63); also by oxidation of *iso*butylene by means of potassium permanganate in neutral aqueous solution (Wagner, Ber. 21, 1232).

4. *Symmetrical dimethylethylene glycol, βγ-dihydroxybutane* $CH_3·CHOH·CHOH·CH_3$; b.p. 183°–184°. Formed by heating for 6 or 7 hours 1 vol. of symmetrical dimethylethylene oxide C_4H_8O with 3 vols. of water to 100° (Eltekow, Chem. Soc. Abstr. 1883, 566).

5. *Tetramethylene glycol, aδ-dihydroxybutane* $OH·(CH_2)_4·OH$; boils at 203°–205°; sp.gr. 1·0111 (Dekkers, Chem. Soc. Abstr., 1891, 164).

6. A-*butylene glycol*, differing from the above, boiling at 183°–184°; has also been prepared by Wurtz (Ann. Chim. Phys. [3] 55, 452); sp.gr. 1·048 at 0°.

7. *a-Methyl propanediol*

$$OH·CH_2·CH(CH_3)·CH_2OH$$

(Henry, Bull. Soc. chim. [3] 13, 1002 Cesaro, Chem. Zentr. 1897, ii. 179).

Butylene diiodide, *aγ-diiodobutane*

$$CH_3·CHI·CH_2·CH_2I;$$

sp.gr. 2·291. From *β*-butylene glycol and hydriodic acid (Wurtz, Bull. Soc. chim. 41, 362).

Isobutylene dinitrite $C_4H_8(NO_2)_2$. By treatment of *iso*butylene with concentrated nitric acid (Haitinger, Monatsh. 2, 287). Forms a crystalline mass. Probably the same body was obtained by Beilstein and Kurbatow (Ber. 14, 1621) by treating the petroleum of Tiflis (b.p. 40°–50°) with nitric acid (sp.gr. 1·52). It formed needles which melted at 96°. They were insoluble in water, but soluble in alcohol and ether.

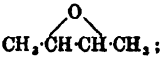
Butylene oxides C_4H_8O.

1. *Isobutylene oxide*

$$(CH_3)_2\overset{\quad O \quad}{C\text{——}CH_2};$$

b.p. 51°–52°; sp.gr. 0·8311 at 0°. From the chlorhydrin C_4H_9ClO, and potash (Eltekow, Chem. Soc. Abstr. 1883, 566).

2. *s-Dimethylethylene oxide*



$$CH_3·\overset{\quad O \quad}{CH·CH}·CH_3;$$

b.p. 56°-57°; sp.gr. 0·8344 at 0°. [illegible] the chlorhydrin (prepared from the symmetrical dimethyethylene and hypochlorous acid) and potash (Eltekow, Chem. Soc. Abstr. 1883, 566).

BUTYRALDEHYDE. *Butyric aldehyde* C_4H_8O. This compound exists in two isomeric forms, termed normal and *iso*butyric aldehyde respectively.

Normal butyraldehyde $CH_3·(CH_2)_2·CHO$ is formed together with acetaldehyde and propaldehyde by the action of chromic acid upon fibrin, casein, and albumen (Guckelberger, Annalen, 64, 39). It is readily prepared by distilling a mixture of calcium formate (2 mols.) and calcium butyrate (1 mol.) in quantities of 50 grams at a time with twice the weight of iron filings. The distillate is fractionated, the fraction 70°–110° treated with sodium hydrogen sulphite (bisulphite), then shaken with ether to extract impurities, and finally distilled with excess of soda (Lipp, Annalen, 211, 355; Linnemann, *ibid.* 161, 186; Kahn, Ber. 1885, 3364). Bodroux has applied Grignard's reagent to a solution of orthoformic and acetaldehyde, thereby obtaining a 75 p.c. yield of butyraldehyde (Chem. Zentr. 1904, i. 1077).

Properties.—Normal butyraldehyde is a liquid which boils at 73°–74° (Lipp, at 73°–77°) and has a sp.gr. 0·8170 at 20°/4° (Brühl, Annalen, 203, 18). It is soluble in 27 parts of water. With sodium hydrogen sulphite (bisulphite) it unites, yielding a crystalline compound (Justin, Ber. 1884, 2505). When treated with aqueous ammonia at 0°, it yields butyraldehyde-ammonia $C_4H_{11}NO,3\frac{1}{2}H_2O$, which crystallises in acute rhombic tetrahedra and melts at 30°–31° (Guckelberger). If, however, alcoholic ammonia and the aldehyde are allowed to stand for a month, and then heated for a day at 100°, condensation occurs, and, after removal of ammonia, alcohol and unattacked butyraldehyde by distillation, two bases, tetrabutyraldine and dibutyraldine $C_8H_{17}NO$ can be separated by fractional precipitation with platinic chloride. The latter only can be crystallised, and when heated is converted into paraconine $C_8H_{15}N$ and water (Schiff, Annalen, 157, 352). The trichlorobutyraldehyde (butylchloral) and its hydrate have been prepared by Pinner (Annalen, 179, 26).

***Iso*butyraldehyde** $(CH_3)_2CH·CHO$ can be prepared by the oxidation of *iso*butyl alcohol with potassium dichromate and sulphuric acid (Lipp, Annalen, 205, 2; Pinner, Ber. 5, 699; Fossek, Monatsh. 2, 614; 4, 661), or by distilling calcium formate with calcium *iso*butyrate (Linnemann and Zotta, Annalen, 162, 7). It dissolves in 9 parts of water at 20°, and is soluble in alcohol and ether. The boiling-point is 63°–64° at 757 mm. (Brühl, Annalen, 203, 18), and the sp.gr. 0·7938 at 20°/4° (Brühl), 0·79722 at 15° (Perkin, Chem. Soc. Trans. 1884, 476). Condensation compounds have been obtained by Perkin (Chem. Soc. Trans. 1883, 91).

BUTYRIC ACID $C_4H_8O_2$. Two isomeric forms of this acid are known, normal butyric and *iso*butyric acid.

Normal butyric acid $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$

Occurrence.—In ordinary butter in combination with glycerol to the extent of 2 p.c.; also in the fruits of *Heracleum villosum* (Fisch) and of *Peucedanum sativum* (Benth. Cl. Hook, *f.*) as hexyl butyrate and octyl butyrate respectively; in the oil of *Eucalyptus Perriniana* as *n*-butyl butyrate (Smith, J. Roy. Soc. New South Wales, 1914, 48, 464). Butyric acid is also found in flesh juice, and is frequently a constituent of decomposing organic matter (*v.* art. FERMENTATION) (J. 1857, 353, 402, 403, 559; 1858, 231; 1859, 363, 364; 1861, 454; 1866, 311). The occurrence of butyric acid in sour milk is treated of by Thorpe (Chem. Zentr. 1909, ii. 1774).

Preparation.—(1) Butyric acid is a frequent product of the oxidation of organic substances; casein, fibrin, and albumen, for example, yield this acid among other products on oxidation with manganese dioxide and sulphuric acid (Guckelberger, Annalen, 64, 68).

(2) All amylaceous and saccharine substances which yield lactic acid as a product of their fermentation can undergo a further fermentation to butyric acid, and this fact is made use of for the preparation of the acid. 5 kilos. of rice or potato starch are boiled with 60 litres of water for some hours, allowed to cool, and the product after 24 hours is treated with 60 grams of malt stirred up with 2 litres of milk, with 1 kilo. of finely divided flesh, and with 2 kilos. of chalk, the chalk being added to neutralise the lactic and butyric acids as rapidly as they are formed, and the whole is allowed to remain with occasional stirring for several weeks at a temperature of 25°–30°. When the evolution of gas has ceased, the product is heated to 80°, filtered, precipitated with sodium carbonate to decompose the calcium salt, again filtered, evaporated to a small bulk, and treated with sulphuric acid. The oily layer of acid so obtained is fractionated to free it from the acetic and caproic acids formed simultaneously, and the fraction 155°–174° is extracted with water, which dissolves the butyric acid but leaves the caproic acid undissolved; the aqueous extract is then neutralised with lime, the solution concentrated, and the salt finally decomposed by hydrochloric acid (Grillone, Annalen, 165, 127).

(3) In the presence of a schizomyces—the so-called *Bacillus subtilis*, which can readily be obtained by stirring hay in water, straining the liquor through a sieve, and boiling for 5 minutes—Fitz (Ber. 11, 52) has found that starch readily undergoes fermentation, yielding normal butyric acid as chief product.

Butyric acid has also been obtained by the fermentation of glycérol in 3 p.c. aqueous solution with a species of schizomyces (Fitz, Ber. 9, 1348; 10, 276), and has been prepared by various synthetical methods (Frankland and Duppa, Annalen, 138, 218; Geuther and Frölich, *ibid.* 202, 306). (For conditions affecting the production of butyric acid by fermentation, see FERMENTATION.)

Properties.—Butyric acid is a colourless, transparent liquid, having an odour resembling that of rancid butter, and a sour burning taste. Cooled to −19° it solidifies, and the crystals melt at about −2°. The acid boils at 161·5° at 760 mm. (Kahlbaum, Ber. 16, 2480); at 162·3° (corr.) (Linnemann, Annalen, 160, 228; Zander, *ibid.* 224, 64); 162·02 (corr.) (Thorpe and Rodger); and has a sp.gr. 0·96704 at 15°/15° (Perkin, Chem. Soc. Trans. 1884, 483), 0·9590 at 20°/4°; μ_D, 1·39906 (Scheig, R. 1899, 169). Butyric acid is inflammable and burns with a blue flame. Alcohol, wood-spirit, and water dissolve it in all proportions, and from the aqueous solution it can be separated by addition of calcium chloride. Prolonged boiling with nitric acid converts it into succinic acid. By the action of calcium carbide, dipropyl ketone may be obtained (Haehn, Chem. Zentr. 1906, ii. 17).

Salts.—The metallic salts of normal butyric acid are generally soluble in water, and are crystalline. $Na\overline{B}$ and $K\overline{B}$ crystalline in indistinct cauliflower-like groups. $Ag\overline{B}$ crystallises in needles or monoclinic prisms, and dissolves in 200 parts of water at 14° (Linnemann and Zotta, Annalen, 161, 177); 100 parts of water dissolve 0·413 part at 16° (Grünzweig, Annalen, 162, 203). $Mg\overline{B}_2,5H_2O$ crystallises in very soluble scales (Pelouze and Gélis, Annalen, 47 249). $Ba\overline{B}_2,4H_2O$ crystallises in nacreous scales, and dissolves in 2·48 parts of water at 14° (Linnemann and Zotta). $Ca\overline{B}_2,H_2O$ crystallises in rhombic forms; 100 parts of water dissolve 19·4 parts at 0°. (For solubility table, *see* Hecht, Annalen, 213, 72.) $Si\overline{B}_2$ forms monoclinic prisms; 100 parts of water at 20° dissolve 39·2 parts of the salt (Grünzweig). $Zn\overline{B}_2,2H_2O$ forms monoclinic prisms; 100 parts of water at 16° dissolve 10·7 parts of the crystallised salt (Grünzweig). $Pb\overline{B}_2$ is an oil which slowly solidifies (Markownikow, Annalen, 138, 361). $Cu\overline{B}_2,H_2O$ crystallises in triclinic forms (Alth, Annalen, 91, 176), and $Cu\overline{B}_2,2H_2O$ crystallises in monoclinic forms (Pelouze and Gélis).

Separation from formic, acetic, and propionic acids.—Mach and Portele (Chem. Soc. Abstr. 1890, 1344) give the following method for the estimation of butyric acid in the presence of acetic acid (as in wine): 500 c.c. of the solution is distilled to a bulk of 125 c.c., diluted to the original volume, and again distilled till only 125 c.c. remains. This is done four times. The total acid in the distillate is estimated by titration with soda or baryta. If soda is used, the neutralised distillate is evaporated down, sulphuric acid is added, and the mixture steam-distilled. The distillate is neutralised with baryta and evaporated so far that it will solidify when cold. The barium butyrate is then extracted with absolute alcohol, and the aqueous solutions of the separated salts treated with sulphuric acid and steam-distilled, the acid in the distillate being subsequently titrated.

The separation of formic, acetic, propionic and butyric acids is also dealt with by Willcox (Chem. Soc. Proc. 1895, 202); Luck (Zeitsch. Anal. Chem. 10, 185); Haberland (*ibid.* 1899, 217); and Muspratt (J. Soc. Chem. Ind. 1900, 204). An expression connecting the percentage of butyric acid in an aqueous distillate with the proportion of the distillate to the original solution is given by Leonard, Smith, and Richmond (Analyst, 1897, 92).

Butyryl chloride, obtained by treating 96 grams of butyric acid with 100 grams of phosphorus trichloride (Burcker, Ann. Chim. Phys. [5] 26, 468); boils at 100°–101·5° (Linnemann); and has a sp.gr. 1·0277 at 23°/4° (Brühl).

Butyric anhydride, prepared by the action of butyryl chloride on butyric acid (Linnemann, Annalen, 161, 179), or by the action of 1 molecule of acetic anhydride or [illegible] mols. sodium butyrate (Michael, Chem. Zentr. 1901, i. 1088), boils at 191°–193° (L.); and has a sp.gr. 0·978 at 12·5° (Gerhardt, Annalen, 87 156).

Butyramide, formed by heating dry ammonium butyrate for six hours at 230° (Hofmann, Ber. 1882, 982); crystallises in tables; melts at 115°; boils at 216° (J. 1856, 516); and is readily soluble in water.

α-Chlorobutyric acid $CH_3\cdot CH_2\cdot CHCl\cdot CO_2H$ is a thick liquid difficultly soluble in water (Markownikow, Annalen, 153, 241).

β-Chlorobutyric acid $CH_3\cdot CHCl\cdot CH_2\cdot CO_2H$, thick liquid (Pinner, Ber. 1879, 2056; 1884, 2008).

γ-Chlorobutyric acid $CH_2Cl\cdot CH_2\cdot CH_2\cdot CO_2H$. Esters only known (Henry, Chem. Zentr. 1898, ii. 273).

αβ-Dichlorobutyric acid $CH_3\cdot CHCl\cdot CHCl\cdot CO_2H$, melts at 72°–73° (Melikow, Annalen, 234, 201; 266, 372).

βγ-Dichlorobutyric acid $CH_2Cl\cdot CHCl\cdot CH_2\cdot CO_2H$; melts at 49°–50° (Lespieau, Compt. rend. 129, 225).

ααβ-Trichlorobutyric acid $CH_3\cdot CHCl\cdot CCl_2\cdot CO_2H$; melts at 60° (Kahlbaum Ber. 1879, 2337: Gargarolli, Annalen, 182, 185).

ααγ-Trichlorobutyric acid $CH_2Cl\cdot CH_2\cdot CCl_2\cdot CO_2H$; melts at 73°–75° (Natterer, Monatsh. 4, 551; 5, 256).

αββ-Trichlorobutyric acid $CH_3\cdot CCl_2\cdot CHCl\cdot CO_2H$; melts at 52° (Szenic and Taggesell, Ber. 1895, 2665).

Tetrachlorobutyric acid $C_4H_4Cl_4O_2$; melts at 140° (Pelouze and Gélis, Arch. Pharm. [3] 10, 434).

Bromobutyric acids have also been obtained by Naumann (Annalen, 119, 120), Schneider (J. 1861, 458), and Michael and Norton (Amer. Chem. J. 2, 16). (*See* also Cloves, Chem. Zentr. 1902, I. 406.)

***Iso*butyric acid** $(CH_3)_2\cdot CH\cdot COOH$.

Occurrence.—*Iso*butyric acid occurs in the fruit of *Siliqua dulcis* (Grünzweig, Chem. Soc. Trans. 1873, 373), and in arnica root (*Arnica montana*) (Sigel, Annalen, 170, 348).

Preparation.—*Iso*butyric acid is most readily prepared by the oxidation of *iso*butyl alcohol with a mixture of sulphuric acid and potassium dichromate. Pierre and Puchot (Ann. Chim. Phys. [4] 28, 366) give the following proportions: *Iso*butyl alcohol (300 parts) is mixed with water (1500 parts) and sulphuric acid (540 parts) and into the well-cooled mixture finely powdered potassium dichromate (400 parts) is gradually introduced. An ethereal layer separates, consisting of *iso*butyl *iso*butyrate, which is decomposed by allowing 55 parts to fall slowly on 100 parts of caustic potash to which one-tenth its weight of water has been added; the resulting potassium salt is then distilled with dilute sulphuric acid, and the aqueous acid purified by fractional distillation.

Synthetical methods for preparing this acid (Annalen, 138, 337), and Markownikow (Annalen, 138, 361).

Properties.—*Iso*butyric acid resembles its isomeride in appearance, but has a less disagreeable odour. It boils at 152° at 760 mm. (Kahlbaum, Ber, 16, 2480); at 153·5°–153·8° at 750·3 mm. (Brühl, Annalen, 200, 180); at 15[illegible]°–154·2° (Zander, *ibid.* 224, 77); 154·0° (corr.) (Thorpe and Rodger); sp.gr. 0·965 at 0° (Zander); 0·9503 at 20° (Linnemann, Annalen, 162, 9). It dissolves in five times its volume of water (L.). The metallic salts of *iso*butyric acid are more soluble in water than those of the normal acid. The potassium and sodium salts form cauliflower-like masses. $Ag\bar{B}$ crystallises in characteristic tabular forms; 100 parts of water dissolve 0·928 part at 16° (Grünzweig, Annalen, 162, 210). $Mg\bar{B}_2$ forms white scales. $Ca\bar{B}_2,5H_2O$ forms four-sided monoclinic crystals; 100 parts of water at 18° dissolve 36 parts of crystallised salt (G.), and the solubility increases as the temperature rises. $Sr\bar{B}_2,5H_2O$; 100 parts of water at 17° dissolve 44·1 parts of the crystallised salt (G.). $Ba\bar{B}_2,\frac{1}{2}H_2O$ forms monoclinic crystals (Fitz, Ber. 1880, 1316). $Zn\bar{B}_2,H_2O$; 100 parts of water at 19·5° dissolve 17·3 parts of the crystallised salt (Grünzweig). $Pb\bar{B}_2$ crystallises in rhombic tables and dissolves in 11 parts of water at 16°.

***Iso*butyryl chloride**, prepared by treating *iso*butyric acid (12 parts) with phosphorus trichloride (7 parts), and subsequently distilling (Tönnies and Staub, Ber. 1884, 850); boils at 91·5°–92·5° at 748·2 mm.; and has a sp.gr. 1·0174 at 20°/4° (Brühl, Annalen, 203, 20).

***Iso*butyryl anhydride**, obtained by boiling *iso*butyric acid with *iso*butyryl chloride for 12 hours in a reflux apparatus and fractionating the product (Tönnies and Staub, Ber. 1884, 850); boils at 181·5° at 734 mm.; and has a sp.gr. 0·9574 at 16·5°.

***Iso*butyramide**, formed by heating dry ammonium *iso*butyrate at 230° for six hours; melts at 128°–129° (Hofmann, Ber. 1882, 982).

α-Chloro*iso*butyric acid $(CH_3)_2CCl\cdot CO_2H$; melts at 31° and boils at 118° (Henry, Bull. Soc. chim. 26, 24; Balbiano, Ber. 1878, 1693).

αβ-Dichloro*iso*butyric acid $CH_3\cdot CH(CH_2Cl)\cdot CCl\cdot CO_2H$ (Brochet, Ann. Chim. Phys. [7] 10, 375).

Trichlor*iso*butyric acid $C_4H_5Cl_3O_2$; melts at 50° (Gottlieb, J. pr. Chem. [2] 12, 1).

Bromo*iso*butyric acids have been prepared by Markownikow (Annalen, 153, 229); Engelhorn (*ibid.* 200, 65, 68); Cahours (*ibid.* Supplt. 2, 349, 352).

Butyric esters. These compounds are for the most part prepared by the action of butyric acid on the corresponding alcohols in presence of some dehydrating agent such as sulphuric acid, the temperature being raised eventually to complete the reaction. Butyric esters are liquids which dissolve in alcohol and ether in all proportions, but are only very sparingly soluble in water. On saponification with caustic potash they yield the corresponding alcohol and potassium butyrate.

Methyl butyrate $C_4H_7O_2Me$, prepared similarly to the ethyl ester, is a colourless liquid with a pleasant odour resembling that of pinemann, Pogg. Ann. [2] 12, 41]; and has a sp.gr. 0·9194 at 0°/4° (Elsässer, Annalen, 218, 314).

Ethyl butyrate, *butyric ether*, is prepared by adding 1 part by weight of sulphuric acid to 2 parts each by weight of butyric acid and alcohol. The liquid becomes heated, and the mixture at once separates into two layers of which the upper one consists of ethyl butyrate. To complete the reaction it is necessary to heat the product at about 80° for a short time. The upper layer is separated, washed with water, dried over calcium chloride, and distilled. The presence of considerable quantities of water does not seem to hinder esterification (Pelouze and Gélis, Annalen, 47, 250).

Ethyl butyrate is a colourless liquid having an odour like that of pine-apples. It boils at 119·9° at 760 mm. (Schumann); and has a sp.gr. 0·8996 at 0°/4° (Elsässer), b.p. 120·0°–120·5°; sp.gr. 0·8784 20°/4° (Matthews and Faville, J. Phys. Chem. 1918, 22, 1). A solution of ethyl butyrate is used in perfumery and in confectionery under the name of pine-apple oil.

Propyl butyrate boils at 142·7° at 760 mm. (Schumann); and has a sp.gr. 0·8930 at 0°/4° (Elsässer).

***Iso*propyl butyrate** boils at 129° at 755 mm.; and has a sp.gr. 0·8787 at 0° (Silva, Ber. 1869, 283), 0·9027 at 0° (Přibram and Handl, Monatsh. 2, 690).

Butyl butyrate boils at 164·8° (corr.), and has a sp.gr. 0·8760 at 12° (Linnemann, Annalen, 161, 195; compare also Lieben and Rossi, *ibid.* 158, 170).

***Iso*butyl butyrate** boils at 156·9° at 760 mm. (Schumann); and has a sp.gr. 0·8798 at 0°, 0·8664 at 16° (Grünzweig, Annalen, 162, 207).

***Iso*amyl butyrate** boils at 178·6° at 760 mm. (Schumann); and has a sp.gr. 0·8823 at 0°/4° (Elsässer).

The hexyl- and octyl-butyrates occur in the oils from the fruits of *Heracleum giganteum* (Franchimont and Zincke, Ber. 4, 824) and *Pastinaca sativa* (Renesse, Annalen, 166, 80) respectively.

Ethereal salts of *iso*butyric acid have been prepared:

Methyl *iso*butyrate boils at 92·3° at 760 m.m. (Schumann); and has a sp.gr. 0·9112 (Elsässer).

Ethyl *iso*butyrate boils at 110·1° at 760 mm. (Schumann); its sp.gr. is 0·8903 (Elsässer).

Propyl *iso*butyrate boils at 133·9° at 760 mm. (Schumann; its sp.gr. is 0·8843 (Elsässer).

***Iso*propyl isobutyrate** boils at 118°–121° at 727 mm.; and has a sp.gr. 0·8787 at 0° (Přibram and Handl).

***Iso*butyl *iso*butyrate** boils at 146·6° at 760 mm. (Schumann); its sp.gr. at 0° 0·8752 (Grünzweig).

***Iso*amyl *iso*butyrate** boils at 168·8° at 760 mm. (Schumann); and has a sp.gr. 0·8759 at 0°/4° (Elsässer).

λ-BUTYROBETAINE *v.* BETAINES.

BUTYROLACTONE *v.* HYDROXYBUTYRIC ACIDS.

BUTYRONE. *Dipropyl ketone* $C_7H_{14}O$.

Butyrone is obtained by distilling calcium butyrate, or preferably a mixture of calcium butyrate and calcium carbonate (Schmidt, Ber. 5, 597); the crude product is dehydrated by treatment with calcium chloride, and purified by fractional distillation. Butyrone boils at 144°, and has sp.gr. 0·8195 at 20°, does not combine with ammonia or sodium hydrogen sulphite (bisulphite), yields a mixture of propionic and butyric acids on oxidation with chromic acid, and is converted into a secondary alcohol $C_7H_{16}O$ and butyrone-pinacone $C_{14}H_{30}O_2$ on treatment with sodium amalgam and water (Kurtz, Annalen, 161, 205).

An isomeride *di-isopropylketone* can be prepared by distilling calcium *iso*butyrate (Münch, Annalen, 180, 327); it boils at 124°–126°, has a sp.gr. 0·8254 at 17°, and does not combine with sodium hydrogen sulphite.

BUTYRO-REFRACTOMETER *v.* REFRACTOMETERS.

BUXIN. An alkaloid obtained from the box-tree (*Buxus sempervirens*). Hager (Chem. Zentr. 1877, 119) found it in beer as an adulterant. It is said by Walz (N. J. P. 14, 15) to be identical with bebeerine (*q.v.*).

BYNIN. Trade name for liquid malt extract.

C

CABBAGE, *Brassica oleracea.* This plant has been modified by careful selection and cultivation so as to produce several apparently very different varieties:

1. Those which form a compact head by overlapping of the leaves, as in the ordinary cabbage.
2. Those of a straggling, open habit of growth, with a branching stem but no distinct 'heart' or head, *e.g.* thousand-headed kale.
3. Those in which a dense head of imperfect flowers are formed, as cauliflower and broccoli.
4. Those in which the stem is enormously developed so as to form a globe, as in kohl-rabi.
5. Those in which a large number of small 'heads' are formed on a tall stem—Brussels sprouts.

Of the cabbage itself, there are many varieties, differing in size, shape, and colour.

Like all the members of the *Cruciferæ*, cabbages contain sulphur compounds, some of which easily undergo decomposition with production of sulphuretted hydrogen.

The average composition of cabbages, as used for cattle food, is, according to Kellner—

Water	Protein	Fat	Sol. carbohydrates	Fibre	Ash
84·7	2·5	0·7	8·1	2·4	1·6

whilst, according to American analyses, the edible portion of culinary cabbages contains:

Water	Protein	Fat	Sol. carbohydrates Fibre	Ash
90·3	2·1	0·4	5·8	1·4

Included in the carbohydrates mannitol and glucose have both been detected (Bysolt, J. Laudw. 1914, 62, 117).

Cabbages, as a farm crop, respond to liberal manuring, and in inland districts are benefited by a small dressing of the soil with common salt. They do best, as a rule, on heavy land, and are usually transplanted from seed-beds.

Formentated cabbage (sauerkraut) yields acetic and propionic acids with occasional traces of formic acid together with an inactive form of lactic acid. Ethyl and propyl alcohols are also formed together with small quantities of esters (Nelson and Beck, J. Amer. Chem. Soc. 1918, 40, 1001).

CACAO BUTTER (spelt also Cocoa Butter), is expressed from the cacao bean, the seeds of the cacao tree, *Theobroma cacao* (Linn.).

The cacao tree is indigenous to the West Indies, but has been introduced into various tropical countries, especially Central and South America and to the West Coast of Africa and the islands in the Bay of Benin. It has also been introduced into Nigeria, and an inducement has been held out by the Government to the Nigerian peasants to grow cacao. As the beans are chiefly worked up for the preparation of cacao, the cacao butter must be considered, to some extent, a by-product of the chocolate industry. For the production of cacao butter, the beans are roasted over a coke fire, and the husks are separated by winnowing. The kernels thus laid bare are ground under millstones and reduced to a paste, when the bulk of the fat is removed by hot expression in hydraulic presses. As the fat in the bean has undergone slight hydrolysis, it is usual to add a carbonate, either of potassium or ammonium, to the beans before roasting. Hence, in the examination of cacao butter, the presence of ammonia or potash soap may be expected.

In Cook's patent process (U.S. Pat. 1006913, 1911) the roasted beans are decorticated, and then pressed sufficiently to powder the mass, and express part of the fat.

A special form of press for separating the fat from the beans has been devised by Hänel (Eng. Pat. 3188, 1915).

The average composition of the cacao bean is, according to König, as follows :—

	Per cent.
Fat	49·0
Water	5·4
Proteins	12·8
Carbohydrates . . .	25·7
Crude fibre . . .	3·71
Ash	3·41

The composition of the shell is as follows :—

Fat	4·21
Water	11·19
Proteins	13·61
Carbohydrates . . .	43·95
Crude fibre	17·63
Ash	9·88
	100·47

The proportion of fat in the bean varies from about 50 to 56 p.c. In the production of cacao powder, only a portion of the cacao butter is expressed, whereas the beans intended for the manufacture of *best* chocolate are not expressed, so that the full amount of fat is allowed to remain in the ground mass. Manufacturers of cheap chocolates remove a portion of the costly cacao butter by expression, replacing it by cheaper substitutes (*see* CHOCOLATE FATS). The kernels contain a small amount of theobromine, a portion of which passes into the cacao butter on expression.

Cacao butter has a yellowish-white colour, turning white on keeping, an agreeable taste and pleasant odour, recalling that of chocolate. At the ordinary temperature, the fat is somewhat brittle. It appears to consist, to a very large extent, of oleodistearin and oleodipalmitin. The solid acids of cacao butter consist of stearic and palmitic acids; small quantities of arachidic acid are stated to occur also amongst the solid fatty acids.

The proportion of stearic acid in the fat is as high as 39–40 p.c. Amongst the liquid fatty acids there seem to be present about 6 p.c. of acids less saturated than oleic acid, most likely linolic acid. From the iodine value of the cacao butter, viz. 32–42, the conclusion may therefore be drawn that it contains not more than about 30 p.c. of oleic acid. The unsaponifiable matter of cacao butter amounts to less than 1 p.c. Matthes and Rohdich (Ber. 1908, 41, 19) found in the unsaponifiable matter a hydrocarbon (most likely identical with amyrilene), stigmasterol, and a phytosterol melting at 130°.

In the older literature the statement frequently occurs that cacao butter does not turn rancid. But it is a matter of common experience that cacao butter, exposed to light and air at the ordinary temperature, becomes rancid in the course of time. Equally erroneous is the statement that rancid cacao butter is obtained from mouldy beans. Most shipments of cacao beans become mouldy in transit, but as the beans in the initial state of manufacture are roasted, the mould is destroyed, so that cacao butter prepared from these beans need not, of necessity readily become rancid. With the growth of the consumption of chocolate and cacao, the trade in cacao beans has become of very great importance.

Holland is the largest exporter of cacao butter, whilst Germany was the largest producer, but exports relatively very little. Of late years the demand for the fat has greatly increased, and the price has risen correspondingly.

Cacao butter, being very high in price, in normal times even higher than cows' butter, is frequently adulterated with, if not completely substituted by, 'chocolate fats.' The adulterants formerly employed, such as tallow and paraffin wax, are easily detected, and hence these adulterants have disappeared. The same holds good of coco-nut and palm-nut stearins, which, for some time, were largely used to adulterate cacao butter. Latterly, adulteration with cacao-shell butter has been practised and is still in vogue; for this purpose, the husks are ground and again expressed, or even extracted with volatile solvents. As the fat thus obtained yields, in analysis, practically the same characteristic numbers as genuine cacao butter itself, chemical analysis alone is unable to reveal adulteration with cacao-shell butter.

Products commercially known as 'green butter' are now extensively used for mixing with cacao butter. They consist of a refined vegetable tallow coloured with chlorophyll or with an aniline dye. The adulteration may be detected by a modification of Halphen's test (J. Pharm. Chim. 1908, 28, 345). On adding bromine to a solution of the fat in carbon tetrachloride, pure cacao butter immediately gives a turbidity, whilst in the case of 'green butter' the liquid remains clear (Revis and Bolton, Analyst, 1913, 38, 201).

Cacao butter, being chiefly produced as a by-product in the manufacture of cocoa, is obtainable in large quantities: it is at present mainly used in the manufacture of cheaper chocolate. Smaller quantities are used in confectionery, in pharmacy for making suppositories and nitroglycerin tablets, and in the 'enfleurage' process of preparing delicate ethereal oils. J. L.

CACHALOT OIL. Oil obtained from the blubber of the cachalot. (For its properties and composition, v. Fendler, Chem. Zeit. 1905, 29, 555.)

CACODYLIAGOL. Syn. for guaiacol cacodylate.

CACODYLIC ACID and **CACODYLATES** v. ARSENIC, ORGANIC COMPOUNDS OF.

CADAVERINE v. PUTREFACTION BASES.

CADE, OIL OF v. JUNIPER.

CADIE GUM v. GUMS.

CADINENE v. TERPENES, JUNIPER.

CADMIUM, (*Kadmium*, Ger.) Sym. Cd. At. wt. 112·3 (Quinn and Hulett); 112·42 (Baxter and Hartmann); 112·32 (De Coninck and Gérard).

Cadmium occurs in small quantities as sulphide in *Greenockite* at Bishopton, Renfrewshire, and in Pennsylvania and Bohemia. This is the only ore containing cadmium as the principal element. Cadmium occurs in small quantities in nearly all zinc ores, but the percentage is considerably lower than that usually stated. Jensch and Kliecisen have shown that the cadmium in zinc ores averages about 0·1 p.c., 0·5 p.c. being only reached in the richest samples, though occasional specimens are stated to have yielded considerably higher values. It occurs also in the silicate and carbonate of zinc at Freiberg, Derbyshire, and Cumberland, and in most commercial zinc.

Preparation.—In the reduction of zinc ores, the first portions of the distillate consist of a mixture of the metals zinc and cadmium and their oxides, but containing a higher percentage of cadmium (on account of its greater volatility) than the original ore, and by further similar treatment it is still further increased. When sufficiently rich, it is used for the extraction of the cadmium. At Silesia, the first portion of the distillate, which contains from 2 to 6 p.c. of cadmium, is mixed with about one-fourth of its weight of coal, and distilled at a dull-red heat; the cadmium then distils with a little zinc, but the greater part of the latter metal remains behind. The cadmium is purified by fractional distillation until a product of 99·5 p.c. or more is obtained; it is then cast into small cylinders about ½ inch thick.

The chief output of cadmium comes from Silesia. A little cadmium is recovered in this country in the purification of zinc sulphate, in the manufacture of lithopone, or from baghouse dusts at lead smelters. Another source which may become important in view of the increasing number of electrolytic zinc plants is the precipitate obtained in purifying the electrolyte prior to deposition of the zinc, as well as the anode mud. Flue dust from brass works contains as much as 2–3 p.c. of cadmium. The supply can easily be increased to meet any reasonable demand.

Various wet methods for the extraction of the cadmium from the concentrated flue dust have been proposed and tried. Some of these are dependent on the precipitation of cadmium from acid solutions by means of zinc; others on the solubility of zinc in neutral ammonium carbonate.

Electrolytic methods for the refining of cadmium are employed, the cadmium being deposited on platinum electrodes and distilled *in vacuo*.

Properties.—Cadmium is a white metal with a tinge of blue, of strong lustre, and capable of taking a high polish. It produces a metallic streak on paper like lead, but less readily. Cadmium is compact in texture and of fibrous fracture, harder and more tenacious than tin; it may be drawn into thin wire or hammered into leaves, but when heated to 80° it becomes brittle, and may be powdered in a mortar. On account of its crystalline structure, it crackles, like tin, when bent.

By distillation in a current of hydrogen, cadmium may be produced in regular octahedra and other forms of the cubic system.

Cadmium melts at 321·7° (Holborn and Day); 320·9° (Holborn and Henning), and boils at 765·9° under a pressure of 760 mm. (Heycock and Lamplough). Its vapour density at 1040° is 3·94 referred to air, or 56·3 referred to hydrogen. Hence it appears that the molecule of cadmium contains but one atom at that temperature, whilst further the values for the latent heat of vaporisation (calculated from the vapour pressure) indicate similar molecular states in liquid and gas (Traube). It is obtained in colloidal solution by electric sparking with a cadmium cathode in water.

According to Demarcay, it emits vapours when heated below the melting-point (Compt. rend. 95, 183). When heated in air, it burns readily, evolving brown fumes of the oxide. Cadmium dissolves in hydrochloric and sulphuric acids with evolution of hydrogen. It is readily attacked by nitric acid. It combines directly with chlorine, bromine, and iodine when placed in solutions of those elements. Cadmium gives a brilliant spectrum of red, green, and blue lines, and its use has been suggested as a convenient standard in refractometry (Lowry).

The salts of cadmium, as a rule, are but slightly dissociated in solution—this is especially so in the case of the iodide—and are hence liable to be incompletely precipitated by reagents.

Detection.—All compounds of cadmium, when heated on charcoal in the reducing flame, give a brown incrustation. Sulphuretted hydrogen produces a yellow precipitate in acid solutions, soluble in strong hydrochloric acid insoluble in alkaline sulphides; it is thus distinguished from antimony and arsenic.

Estimation.—Cadmium may be precipitated as carbonate and weighed as oxide. Owing, however, to the reduction of the oxide and the great volatility of the metal, if filter papers are employed, the results are low, even when careful precautions are taken. A Gooch crucible and asbestos filter should therefore be employed. Cadmium may also be estimated by precipitation from a neutral solution by excess of diammonium phosphate, and, after standing some time, collecting the precipitate on a weighed filter paper, dried at 105° (Page and Miller).

Electrolytic methods of estimation have also been found to be suitable and to yield accurate results. A cyanide solution with an E.M.F. of 3 to 3·5 volts and a current of 0·02 to 0·05 ampere, is a convenient arrangement (Rimbach).

To separate it from other metals not precipitable by sulphuretted hydrogen in acid solution, it is precipitated as sulphide by that gas, washed, dissolved in nitric acid, and precipitated with sodium carbonate.

Alloys of cadmium. The addition of cadmium to metals usually increases their fusibility without destroying their malleability.

The alloys with gold and copper are brittle; the others are usually ductile and malleable. With gold, a crystalline brittle silvery alloy, corresponding with AuCd, has been prepared, and the existence of a compound, Au_4Cd_3, is also indicated. Alloys, containing between 51 and 63 p.c. of cadmium, are very brittle. With platinum, a white crystalline compound appears to exist; and with copper compounds Cu_2Cd and Cu_2Cd_3, are indicated. The alloys rich in cadmium are steel-grey and soft, but become harder and more brittle with increase of copper up to 26·5 p.c., when the hardness again decreases and the yellow colour of copper appears. Researches by Rose on alloys of silver and cadmium indicate the existence of the compounds $AgCd_3$, Ag_2Cd_3, AgCd, Ag_3Cd_2, Ag_3Cd, and Ag_4Cd. Alloys containing over 80 p.c. silver are uniform and homogeneous, and well suited as material for trial plates for silver coinage and ware, for which the silver-copper alloy is not quite satisfactory. With sodium a compound, Cd_2Na, has been prepared, and compounds CdMg and $CdMg_4$ are indicated in the alloys with magnesium. The addition of ¼ p.c. cadmium to zinc increases the breaking strain, but more than ½ p.c. has the opposite effect. The amalgam, with mercury, was formerly used in dentistry, but its use has been discontinued, as it produces discolouration of the dentine. Multiple alloys, containing bismuth, frequently melt below 100°, and are used as fusible alloys; for these and other alloys containing bismuth and cadmium, *v. Alloys of bismuth*, art. BISMUTH. The metal is occasionally used as a substitute for tin in solder.

Cadmium oxide CdO is prepared by heating the carbonate, in which case it is of a pale-brown colour; or by igniting the nitrate, when it is much darker and forms minute crystals. By heating cadmium in a current of oxygen, the oxide may be condensed in octahedral crystals; at low temperatures, some peroxide is also formed (Manchot). Cadmium oxide is infusible, insoluble in water, soluble in acids. It constitutes the brown deposit found in the condensers in the distillation of zinc.

Cadmium suboxide Cd_2O appears to be formed in small quantity when cadmium oxalate is heated in a stream of carbon dioxide (Tanatar, Zeitsch. anorg. Chem. 1901, 27, 433), or when cadmium oxide is heated with carbon monoxide (Brislee, Chem. Soc. Trans. 1908, 93, 162), or by dehydrating cadmious hydroxide, obtained by the action of water on the product formed by fusing cadmium chloride with cadmium (Moore and Jones, Amer. Chem. J. 1890, 12, 488). *Cf.* Denham, Chem. Soc. Trans. 1919, 516.

Cadmium chloride $CdCl_2$ is prepared by evaporating the solution of the metal or oxide in hydrochloric acid. It melts below a red heat and sublimes at a higher temperature, condensing in micaceous plates.

Cadmium iodide CdI_2 is obtained by digesting 1 part of the metal with 2 parts of iodine in water and evaporating the solution. It crystallises in large transparent tablets, soluble in water and alcohol. It is used in medicine and, on account of its stability and solubility in alcohol, for iodising collodion plates in photography.

Cadmium sulphide. *Cadmium yellow, Jaune brillant.* This pigment may be produced by the addition of sulphuretted hydrogen or an alkaline sulphide to a solution of a cadmium salt. It may also be prepared by heating a mixture of cadmium oxide and excess of sulphur, but that produced by the former method is of a finer colour and has greater covering power. It may also be formed by the action of hydrogen sulphide on cadmium vapour. The various hues of different preparations depend on whether the substance is crystalline or amorphous, and on the size and nature of the surface of the grains.

It is an orange- or lemon-yellow powder, but may be obtained in prismatic crystals of sp.gr. 4·82. When heated to redness, it becomes first brown, then carmine; it melts at a bright-red heat, and solidifies, on cooling, in laminæ of the original colour.

It is a very brilliant permanent colour. According to Jacquet, it is acted upon by light and by chlorine. It is much used as an oil and water colour, for colouring certain toilet soaps, for the production of a blue flame in pyrotechny, and in calico printing. The chief adulterants are compounds of zinc. According to Buchner (Chem. Zentr. 15, 329), two modifications exist: (1) the α-variety, precipitated by hydrogen sulphide in faintly acid solution; it is lemon-yellow, and possesses good covering power. When heated, it darkens temporarily to violet-red, but no permanent change occurs unless the temperature is high enough to produce oxidation. (2) The β-variety, produced in strongly acid solution; it resembles red lead, possesses good covering power, and is ordinarily quite permanent; if heated, it changes to the α-variety. Various shades are obtainable by mixture. The sulphide can also be obtained in colloidal solution.

Schmid (Dingl. poly. J. 241, 149), prepares a steam yellow for calico-printing as follows: 16 parts wheaten starch and 40 parts burnt starch are boiled in 1000 parts of water and mixed while hot with 350 parts of sodium thiosulphate. To the cooled solution, 350 parts of finely powdered cadmium nitrate are added with constant stirring until dissolved. This solution does not react in the cold, and may be applied to the fabric and steamed, the yellow sulphide being then precipitated.

Cadmium sulphate $CdSO_4,4H_2O$ is a very soluble salt prepared by dissolving the oxide or carbonate in sulphuric acid. It is used to some extent in medicine in place of zinc sulphate, especially on the Continent. It is also used in the construction of the Weston cell as a standard of E.M.F. The cell is usually made in the form of an H. One of the limbs contains mercury, covered by a paste of cadmium and mercurous sulphates. The other contains cadmium amalgam. Above both, to nearly the top of the limbs, which are closed by cork and wax, is a saturated solution, with crystals of cadmium sulphate. Through the glass of the lower limbs, platinum wires pass. The cell has an E.M.F. of 1·019 volts at 15°–18°, and has the advantage of a very low temperature coefficient.

Forms a double salt with ammonium sulphate $CdSO_4(NH_4)_2SO_4 6H_2O$. A salt of the composition $2CdSO_4(NH_4)_2SO_4$, hygroscopic, microscopic crystals, yellow when hot, white when cold, of sp.gr. 3·11 at 22° is also known (Veres, Compt. rend. 1914, 158, 39).

Cadmium nitrate $Cd(NO_3)_2,4H_2O$ is prepared by dissolving the oxide or carbonate in nitric acid. It crystallises in deliquescent fibrous needles, soluble in alcohol.

Cadmium salicylate is prepared from the acid and oxide or carbonate. It is readily soluble in alcohol, ether, or glycerol, and is used in medicine as an external antiseptic.

CÆSIUM. Symb. Cs. At. wt. 132·8. Cæsium was discovered in 1860 by Bunsen and Kirchhoff, in the Durkheim water, being the first element detected by means of the spectroscope.

It is widely but sparsely distributed, usually in association with rubidium, as in the *lepidolite* from Hebron in Maine, U.S.A., which contains 0·4 p.c. cæsium oxide and 0·2 p.c. rubidium oxide; in *petalite*; in the mother liquors of the Nauheim salt spring, and in the ash of seaweed, tobacco, tea, and other plants. Setterberg (Annalen, 210, 100) describes a method for the separation of cæsium and rubidium from the alums obtained as a by-product in the manufacture of lithia from lepidolite. For observations on the solubilities of cæsium alum, *see* Hart and Huselton (J. Amer. Chem. Soc. 1914, 36, 2082). For details of the method of separation of cæsium and rubidium by fractional crystallisation of the aluminium and iron alums, *see* Browning and Spencer (Amer. J. Sci. 1916, 42, 279). Cæsium and rubidium chlorides are also obtained from carnallite by repeated fractional crystallisation. The cæsium is separated from the rubidium by the addition of antimony chloride, which precipitates only the cæsium in the form of the double salt $SbCl_3·6CsCl$ (Fict and Kubeirscky).

Cæsium occurs free from rubidium in the rare mineral *pollucite*, from Elba, to the extent of 34 p.c. of cæsium oxide; to the extent of 1·71 parts of cæsium chloride per million in the water of the Wheal Clifford Mine (Yorke), and in the mineral waters of Frankhausen.

Cæsium may be prepared by electrolysis of a fused mixture of cæsium cyanide 4 parts and barium cyanide 1 part, using electrodes of aluminium (Setterberg). It is more readily obtained by heating the hydroxide with aluminium in a nickel retort, and condensing the metal in a glass receiver (Békétoff); or by heating the carbonate or hydrate with magnesium in a current of dry hydrogen (Graebe and Eckhardt). A more rapid method, giving a better yield, is stated to be the reduction by calcium; 3 grams of this metal in small pieces with 12 grams of cæsium chloride are heated in a wide inverted Y-tube, the vertical limb being connected to a Sprengel pump. Reduction occurs at about 400°, and the cæsium volatilises and condenses in the vertical tube. It resembles rubidium and potassium in appearance, being silvery white, and soft at ordinary temperatures. It quickly oxidises in air, and decomposes water at –116° with ignition of the liberated hydrogen at higher temperatures. Its sp.gr. at 15° is 1·88, 1·0029 (Hackspill, Compt. rend. 1911, 152), its melting-point is 26°–27° (Setterberg); 28·45° (Rengade, Compt. rend. 1913, 156, 1897).

The coefficient of expansion of the solid metal is 0·000291, of the liquid metal 0·000345 between 28° and 50° (Hackspill, *l.c.*). Specific heat (solid) $0·0522+0·000137t$; liquid $0·0604-0·000034t$; heat of fusion 3·766; ratio of atomic heat of fusion to abs. m.p.=1·66 (Rengade).

Cæsium is the most electro-positive of all the elements. Its salts are stable and have a strong tendency to form double salts. The salts are isomorphous with those of potassium and rubidium, and impart a more reddish tinge to the bunsen flame than salts of those metals. The hydroxide CsHO is a greyish-white highly deliquescent solid, melting below a red heat. The oxide Cs_2O is prepared by exposing the metal to insufficient oxygen and distilling off excess of cæsium; a peroxide CsO_2 is formed by heating to 300° in excess of oxygen (Rengade). For its *absorption spectrum*, *see* Bevan (Proc. Roy. Soc. 1911, 85, A, 54).

CAFFEARINE. Found in the mother liquors of caffeine from coffee berries; is identical with trigonelline (*q.v.*) (Gorter, Annalen, 1910, 372, 237).

CAFFEINE AND THE ALKALOIDS OF TEA, COFFEE, AND COCOA. The chief alkaloids of practical importance in this series are caffeine $C_8H_{10}O_2N_4$, theobromine $C_7H_8O_2N_4$, and theophylline $C_7H_8O_2N_4$. Adenine $C_5H_5N_5$, xanthine $C_5H_4O_2N_4$, and hypoxanthine $C_5H_4ON_4$ have also been found in tea in small amounts.

These alkaloids are all derived from a parent substance purine $C_5H_4N_4$, which has not been found occurring naturally, but was synthesised by Fischer (Ber. 1898, 31, 2550). Derivatives of purine occur widely distributed in plants and animals. Of these, uric acid (2 : 6 : 8-trioxypurine) $C_5H_4O_3N_4$ is of considerable importance, as it is used in the industrial manufacture of the alkaloids of this series; guano, in which it occurs in considerable quantities, being the source from which it is obtained. The constitution of these compounds and their relationship to purine and to each other will be considered in detail below.

Caffeine $C_8H_{10}O_2N_4$ is the principal alkaloid of tea and coffee and of similar stimulants, such as kola (West Africa), maté or Paraguay tea, and guarana (both used in South America).

Average samples of tea leaves contain from 2·5 to 3 p.c. of caffeine, though some varieties may contain as much as 4 p.c. Coffee beans, in which caffeine occurs partly free and partly as potassium caffeine chlorogenate, rarely contain more than 1·5 p.c. (*v.* Bull. Imp. Inst.

1908, 6, 1). Maté contains from 1 to 2 p.c., guarana paste from 3 to 4 p.c., and kola about 3 p.c. of caffeine. Only very small amounts occur in cocoa beans (Schmidt, Annalen, 1883, 217, 306).

Caffeine is obtained industrially almost entirely from tea dust or damaged tea. The material is 'denatured' by addition of about 10 p.c. of slaked lime and 0·1 p.c. of assafœtida. The well-mixed material is then extracted either with boiling water or more usually with hot alcohol in a reflux apparatus. The extraction is repeated three or four times, the extracts combined, and the solvent recovered by distillation. The residual liquid is treated with litharge or lead acetate, avoiding excess; the precipitate is filtered off, and the filtrate concentrated, when caffeine crystallises out on cooling. The product is purified by recrystallising, decolourising with charcoal, &c., when necessary, or by sublimation.

An alternative method sometimes employed consists in the exhaustive percolation of the denatured tea by means of hot benzene. The concentrated extract is freed from benzene, the residue, consisting of caffeine, together with fatty and resinous material, is boiled with water and filtered from insoluble material. On concentrating the filtrate caffeine crystallises out, and may be purified by the methods described above.

Caffeine is also a by-product obtained in the manufacture of 'caffeine free' coffee, and is further manufactured synthetically from uric acid (*see* below). For the preparation of small quantities of caffeine, 100 grams of tea dust is extracted three or four times with boiling water. The extracts are combined, 10–15 grams of magnesia added, and the mixture taken to dryness. The residue is transferred to a Soxhlet apparatus and extracted with chloroform. On evaporating off the solvent a somewhat impure caffeine remains, which may be purified by crystallisation from water or by sublimation.

Caffeine crystallises from water with $1H_2O$, from alcohol anhydrous, in long silky needles. It loses water at 100°, and when anhydrous melts at 234°–235°. It sublimes readily at about 180°.

One part by weight of caffeine dissolves in 50 parts of alcohol (90 p.c.), 300 parts of ether, 9 parts of chloroform, or 80 parts of water at about 15°. It is very soluble in hot water (1 : 2), so that a hot concentrated aqueous solution on cooling sets to a solid crystalline mass. Its aqueous solution reacts neutral to litmus.

Caffeine is a weak base. Its salts are dissociated on evaporation of their aqueous solutions, and the free base may be obtained from acid solutions by shaking with chloroform. Certain double salts of caffeine are more stable; the mercurichloride $B{\cdot}HgCl_2$ forms colourless needles, m.p. 246°; the aurichloride $B{\cdot}HAuCl_4{\cdot}2H_2O$, m.p. 243° (248·5° anhydrous), on warming with water forms an amorphous yellow precipitate 'aurichlorcaffeine,' $C_8H_9(AuCl_2)O_2N_4$, m.p. 207° (Dunstan and Shepheard, Chem. Soc. Trans. 1893, 63, 199). For other caffeine salts, *see* Nicholson (Annalen, 62, 71) and Schmidt (*ibid.* 1883, 217, 283; and Ber. 1881, 14, 813).

Caffeine citrate, largely used in medicine, is obtained by evaporating an aqueous solution of equimolecular proportions of caffeine and citric acid to dryness. It forms a white powder easily soluble in water. Similar compounds are caffeine sodio salicylate and benzoate, which are also used medicinally.

Caffeine dissolves without colouration in concentrated sulphuric acid or cold concentrated nitric acid. If to the solution in sulphuric acid a crystal of potassium dichromate be added a green colouration is produced. Caffeine, in common with the other alkaloids of this group, gives the murexide reaction. If a small quantity of the base be moistened with concentrated hydrochloric acid a crystal of potassium chlorate added and the mixture evaporated to dryness, a reddish-brown residue is obtained, which, on moistening with dilute ammonia, gives a fine reddish-purple colouration.

Caffeine in dilute acid solution is precipitated by phosphomolybdic and phosphotungstic acids and by potassium bismuth iodide. With tannic acid a precipitate is formed, which is soluble in excess of the reagent. No precipitate is obtained with Mayer's reagent or iodine in potassium iodide.

Estimation. A very large number of processes have been suggested from time to time for the estimation of caffeine in tea, coffee, &c., and widely divergent results have been obtained with methods differing only in minor details. This appears to be due, in many cases, to unsatisfactory preliminary treatment of the material under investigation, the caffeine not being set free from the complex compounds (*e.g.* caffeine potassium chlorogenate) in which it occurs naturally.

Stahlschmidt's process, as modified by Allen, appears to give satisfactory results, and is carried out as follows:—

Six grams of finely-powdered tea are boiled under reflux with 500 c.c. of water for 6–8 hours. The decoction is then filtered and the residue washed with hot water until the volume of the filtrate and washings is 600 c.c. The solution is then heated nearly to boiling, 4 grams of lead acetate added, and the mixture boiled under reflux for 10 minutes. If the precipitate does not coagulate and settle down readily more lead acetate is added and the boiling repeated. The liquid is filtered, 500 c.c. evaporated to 40 c.c., and the caffeine extracted by shaking with chloroform. On evaporating off the solvent caffeine remains behind and is weighed. Tatlock and Thomson (Analyst, 1910, 35, 105) boil 2 grams of tea with 800 c.c. of water for one hour, filter and evaporate to small bulk. The solution is made alkaline with caustic soda, and the caffeine extracted by shaking with chloroform. This method is said to give results identical with those obtained by more complicated processes. Other methods in use are due to Paul and Cownley (Pharm. J. 1887, (iii.) 18, 417); Dvorkowitsch (Ber. 1891, 24, 1945); Keller (Ber. Deut. pharm. Ges. 1897, 7, 105); Power and Chesnut, J. Amer. Chem. Soc. 1919, 41, 1298; and for the estimation of caffeine in coffee a modification of the last method by Kats (*ibid.* 1902, 12, 250).

Theobromine $C_7H_8O_2N_4$ is the principal alkaloid found in cocoa beans in which it is present to the extent of about 1·5–3·0 p.c.

It also occurs in small quantities in kola nuts and leaves, in guarana, and in tea.

For the preparation of theobromine the cocoa beans (commercially the husks which contain about 0·5–1 p.c. of theobromine are employed) are freed from fat as far as possible, either by pressure or by extraction with light petroleum, the residue mixed with half its weight of slaked lime, and the mixture exhausted by boiling alcohol (80 p.c.). A considerable portion of the theobromine separates on cooling, and is filtered off. The filtrate is then acidified, the alcohol removed by distillation, the residual liquid filtered hot, and the filtrate neutralised. Theobromine separates as a yellowish-white crystalline powder. The product is purified by crystallisation from boiling water or alcohol, but best from hot glacial acetic acid. On the large scale purification is most readily achieved by dissolving in alkaline solution and reprecipitating by addition of acid.

Theobromine forms a white crystalline powder which sublimes unchanged at about 290°, and melts at 329°–330°. It is very sparingly soluble in water and most organic solvents. It is soluble in about 20 parts by weight of boiling glacial acetic acid, from which it separates almost completely on cooling. It behaves both as a weak base and an acid. The hydrochloride $B{\cdot}HCl,H_2O$ is crystalline, and is obtained by dissolving theobromine in hot concentrated hydrochloric acid and cooling the solution. On drying at 100° the free base is obtained. Theobromine dissolves in dilute nitric acid, and treated with silver nitrate slowly forms a compound $C_7H_8O_2N_4HNO_3AgNO_3$; if, however, theobromine be dissolved in dilute ammonia, silver nitrate added, and the solution then boiled, a white crystalline precipitate of silver theobromine $C_7H_7O_2N_4Ag{\cdot}1{\cdot}5H_2O$, which is almost insoluble in water, is obtained. Theobromine also forms a calcium salt, which can be crystallised from water.

Theobromine gives the murexide reaction, and is precipitated by the usual alkaloid precipitants, with the exception of Mayer's reagent.

The base finds employment in medicine chiefly as a diuretic, and for this purpose numerous soluble compounds of theobromine have been produced. Chief among these may be mentioned *Diuretin* (theobromine sodium salicylate), prepared by dissolving theobromine in the calculated equivalent amount of caustic soda solution, adding a molecular proportion of sodium salicylate and evaporating the solution to dryness *in vacuo*. *Uropherin* (theobromine lithium salicylate), *Uropherin*-B (theobromine lithium benzoate), and *Barutin* (barium theobromine sodium salicylate), &c., are compounds of the same type.

Estimation. The following process, due to Dekker (Rec. trav. chim. 1903, 22, 143), is generally employed for the estimation of theobromine in cocoa and similar products (*cf.* Débourdeaux, J. Pharm. Chim. 1917, 15, 306).

Ten grams of the powdered material is mixed with 5 grams of magnesia and boiled under reflux for one hour with 300 c.c. of water. The extract is filtered off and the extraction repeated for fifteen minutes with a fresh quantity of water. The filtrates are combined and evaporated to dryness on the water-bath. The residue is mixed with sand, the material transferred to a Soxhlet, and completely extracted with chloroform. On evaporation of the solvent theobromine remains, and is dried and weighed.

A method for the estimation of theobromine depends upon the formation of its periodide $C_7H_8O_2N_4.HI,I_4$. 0·1 gram of the sample with an equivalent quantity of sodium acetate, is dissolved in 2 c.c. of glacial acetic acid, 5 c.c. of hot water are added, and the solution is transferred to a 100 c.c. flask containing 50 c.c. of *N*/10-iodine solution; 20 c.c. of saturated sodium chloride solution and 2 c.c. of conc. hydrochloric acid are added, and after about 18 hours, the mixture is diluted to 100 c.c., filtered, and the excess of iodine titrated in an aliquot portion of the filtrate (Emery and Spencer, J. Ind. Eng. Chem. 1918, 10, 605).

Theophylline $C_7H_8O_2N_4$, isomeric with theobromine, is of much less importance than theobromine and caffeine. It was found in small quantity in tea by Kossel (Zeitsch. physiol. Chem. 1889, 13, 298), and was obtained from the mother liquors from which caffeine had crystallised out. The complete isolation was effected as follows:—

The mother liquors were diluted with water, acidified with dilute sulphuric acid, and filtered after standing for some time. The filtrate was made alkaline with ammonia, silver nitrate added, and the mixture allowed to stand 24 hours. The precipitate was collected and dissolved in warm dilute nitric acid. On cooling the silver compounds of adenine and hypoxanthine crystallised out. To the filtrate from these ammonia was added, and silver theophylline was precipitated. The precipitate was decomposed by sulphuretted hydrogen, and on concentrating the filtrate xanthine and finally theophylline crystallised out. Further quantities were obtained from the mother liquor by precipitation with mercuric nitrate and decomposition of the mercury precipitate.

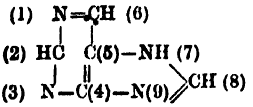
Theophylline crystallises with $1H_2O$ in thin plates or needles, m.p. 264°. It is sparingly soluble in cold, readily soluble in hot, water or alcohol. It behaves as a weak base, and yields salts with acids and derivatives with metals. It gives the murexide reaction, and in general is very similar to theobromine. It forms soluble double salts, of which *theosin* (sodium theophylline sodium acetate) has been successfully employed in medicine as a diuretic.

Adenine $C_5H_5N_5$ (6-aminopurine), as mentioned above, has been found in small quantities in tea. It crystallises with $3H_2O$, sublimes at 250°, and melts at 360°–365°. It is sparingly soluble in cold, readily soluble in hot, water. The picrolonate, m.p. 265°, crystallises from water. Adenine has been synthesised by Fischer (Ber. 1897, 30, 2226), and by Traube (Annalen, 1904, 331, 64).

Hypoxanthine $C_5H_4ON_4$ (6-oxypurine), needles, m.p. 150°, was found in small quantities in tea (Kossel, *l.c.*). Kruger, however (Zeitsch. physiol. Chem. 1895, 21, 274), suggests that it was produced from adenine by the method of isolation employed. It is a weak non-acid base and forms metallic derivatives. It is sparingly soluble in cold, rather more readily soluble in hot, water.

Xanthine $C_5H_4O_2N_4$ (2 : 6-dioxypurine), found to be present in tea (Kossel, *l.c.*), has similar properties to hypoxanthine.

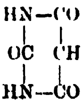
Constitution and Synthesis of Caffeine, Theobromine, and Theophylline. It has been mentioned previously that the alkaloids described above are closely related members of a group of bases derived from a parent substance purine, which has the constitution denoted by the formula shown (Fischer, Ber. 1898, 31, 2550).



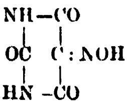
Caffeine, theobromine, and theophylline are, in fact, methylated derivatives of xanthine, which itself is 2 : 6-dioxypurine. Theobromine and theophylline are dimethyl xanthines, from which caffeine and trimethyl xanthine may be obtained by methylation. Thus caffeine is formed when silver theobromine is heated with methyl iodide (Strecker, Annalen, 1861, 118, 170), by heating potassium theobromine with methyl iodide at 100° (E. Schmidt, Annalen, 217, 295), or by the action of dimethyl sulphate upon theobromine in alkaline solution (Ultée, Chem. Wkbld. 1910, 7, 32). The silver compound of theophylline, on treatment with methyl iodide, similarly yields caffeine.

Our knowledge of the constitution of the purine derivatives is largely due to the work of Fischer. One of the most important members of the series is uric acid 2 : 6 : 8-trioxypurine, which occurs naturally in large quantities in guano and serves as a starting-point for the synthetic manufacture of the alkaloids under consideration.

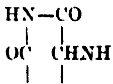
The synthesis of uric acid was accomplished by Fischer and Ach (Ber. 1895, 28, 2473). Malonic acid was condensed with urea to form malonyl carbamide (I.), which, by the action of nitrous acid, yields an *iso*nitroso derivative violuric acid (II.). On reduction uramil (III.) is obtained, which by the action of potassium cyanate is converted into *pseudo* uric acid (IV.). This, on treatment with hot dilute acid, gives uric acid (V.).



I.



II.



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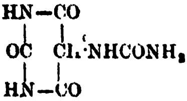
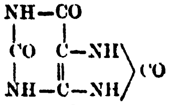
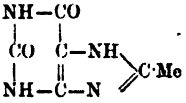


IV.

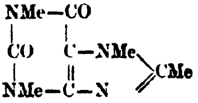


V.

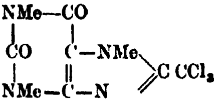
From uric acid caffeine is manufactured synthetically by the following reactions (Boehringer u. Söhne, D. R. P. 121224). Uric acid is converted by heating with acetic anhydride into 8-methylxanthine (VI.). This, on methylation in alkaline solution, gives 1 : 3 : 7 : 8-tetramethylxanthine (VII.). By the action of chlorine under specified conditions this is converted into a trichloro derivative of the constitution shown in formula (VIII.) which, on heating with dilute caustic potash solution, yields caffeine (IX.) Under slightly different conditions a tetrachlor derivative (X.) is obtained, which on treatment with potash yields theophylline (XI.).



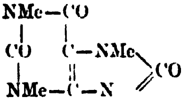
VI.



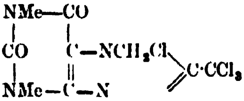
VII.



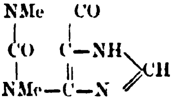
VIII.



IX.

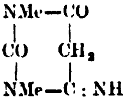


X.

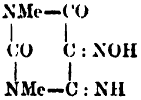


XI.

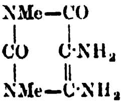
Theophylline (XI.) is also obtained commercially from dimethyl carbamide (Traube, Ber. 1900, 33, 3035). This is condensed with cyanacetic acid in presence of phosphoryl chloride and gives dimethylimino barbituric acid (XII.), which by the action of nitrous acid yields an oximino derivative (XIII.). On reduction a dimethyl-diamino-dioxy-pyrimidine (XIV.) is produced, which with formic acid yields a formyl derivative (XV.). This on heating loses water with formation of theophylline (XI.).



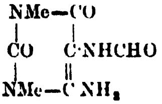
XII.



XIII.

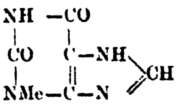


XIV.

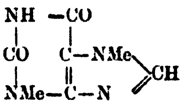


XV.

Theobromine has been synthesised by a series of reactions similar to those above. Starting with methyl carbamide 3-methylxanthine (XVI.) is obtained, which on methylation gives theobromine XVII.

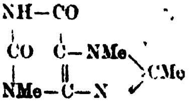


XVI.

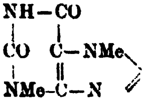


XVII.

Theobromine may also be obtained synthetically from uric acid. This is converted into 8-methylxanthine (VI.) as in the caffeine synthesis. The dry dipotassium salt of 8-methylxanthine is heated with methyl iodide when trimethyl xanthine (XVIII.) is obtained. Chlorination of this compound results in the formation of a trichloro derivative (XIX.), which on heating with dilute caustic potash solution yields theobromine (XVII.).



XVIII.



XIX.

A. J. E.

CAFFEONE (*Caffeol*). A brown oil, heavier than water, and slightly soluble in boiling water. Constitutes the aromatic principle of coffee. May be obtained by distilling freshly roasted coffee with water, and agitating the distillate with ether, which dissolves out the oil. According to Lehmann and Wilhelm (Chem. Zentr. 1898, ii. 372), it has no physiological action on a healthy man (*v.* COFFEE). According to Grafe (Monatsh. 1912, 33, 1389), it consists of about 50 p.c. of furfuryl alcohol and 38 p.c. of valeric and acetic acids, with phenolic substances of a creosote odour and a nitrogenous substance allied to pyridine to which the aroma is due. It appears to be formed by the distillation of the crude fibre of the bean.

CAFFETANNIC ACID *v.* TANNINS.

CAÏL-CEDRA, *Khaya senegalensis* (A. Juss.). A tree of the meliaceous order, growing on the banks of the Gambia and on the lowlands of the peninsula of Cape de Verde. Its bark is very bitter, and is much prized by the natives as a febrifuge, on which account it has been called the *cinchona of Senegal*. Its wood resembles American (Honduras, Cuba, Spanish) mahogany, is one of the so-called African mahoganies, and is used in making the finer kinds of furniture. The bark contains, amongst other substances, an extremely bitter, neutral resinous substance, called cail-cedrin, to which its active properties appear to be due.

Cail-cedrin is very sparingly soluble in water, but readily soluble in alcohol, ether, and chloroform. It is obtained by repeatedly exhausting the coarsely pulverised bark with boiling water; evaporating the filtered liquids over the water-bath to the consistence of a syrup; exhausting this extract with alcohol of 90 p.c.; precipitating the alcohol filtrate with basic lead acetate; filtering, distilling off the alcohol, and agitating the residue with chloroform, which dissolves nothing but the bitter principle. 1 kilogram of the bark yields about 8 milligrams of cailcedrin (Caventou, J. Pharm. [3] 16, 355; 33, 123).

CAÏNCETIN *v.* GLUCOSIDES.

CAINCIN *v.* GLUCOSIDES.

CAÏRNGORM *v* QUARTZ.

CAJEPUT or **CAJUPUT OIL** *v.* OILS, ESSENTIAL.

CAJEPUTOL *v.* CAMPHORS.

'CAL' *v.* TUNGSTEN.

CALABAR BEAN *v.* ORDEAL BEAN.

CALABAR FAT *v.* PHYSOSTIGMINE.

CALABARINE, CALABAROL, *v.* ORDEAL BEAN.

CALAFATITE. A double sulphate of aluminium and potash, so named after its discoverer, Calafat. Occurs near Almeria. Contains SO_4 34·77, Al_2O_3 37·98, K_2O 9·64, H_2O 17·61, sp.gr. 2·75. (*V.* ALUNITE.)

CALAMINE (*Galmei*, Ger.). Under this name two common zinc minerals—the carbonate (*v.* Smithsonite) and the hydrous silicate (*v.* Hemimorphite)—are frequently much confused. The Latin form *lapis calaminaris* is supposed to be a corruption of the old name *cadmia* (καδμία) used for zinc ores in general. The minerals in question often so closely resemble one another in external appearance that it is only possible to distinguish them by chemical tests; and it was not until 1803 that James Smithson definitely established the existence of, the two distinct species. The name calamine was then applied by some authors to the carbonate (sparry calamine), and by other authors to the hydrous silicate (electric calamine). In 1832 F. S. Beudant proposed the name smithsonite for the carbonate, restricting the name calamine to the hydrous silicate; but most unfortunately Brooke and Miller, in 1852, reversed these designations. Beudant has been followed by Dana and many other mineralogists, but in England the name calamine is unfortunately still much in use for the carbonate, and hemimorphite (G. A. Kenngott, 1853) for the hydrous silicate. The use of the latter name partly clears up the confusion, since it is descriptive of the very characteristic hemimorphic development of the crystals. The old name zinc spar is also descriptive of the carbonate. L. J. S.

CALAMUS. The Indian variety of *Acorus calamus* (Linn.); is used as a medicine in the Levant; the Turks candy it and employ it as a remedy against contagion. The volatile oil occasionally enters into the composition of aromatic vinegar. According to Thoms, *cicorin* $C_{36}H_{60}O_6$, in contact with ferments, splits up into sugar and oil of calamus

$$C_{36}H_{60}O_6 = C_6H_{12}O_6 + 3C_{10}H_{16}$$

(*cf.* von Soden and Rojahn, Chem. Zentr. 1901, i. 843; Thoms and Beckstroern, Ber. 1901, 34, 1021) (*v.* ACORUS CALAMUS).

CALAVERITE. A telluride of gold, $AuTe_2$, containing 40-43 p.c. of gold with 1-3 p.c. of silver. It was first found in Calaveras Co., California, and afterwards in considerable abundance in the Cripple Creek district in Colorado and at Kalgoorlie in Western Australia, where it is of importance as a telluride ore of gold. Sp.gr. 9·155-9·39. The small complex (monoclinic or triclinic) crystals from Colorado are tin-white in colour, tarnishing to bronze-yellow on exposure. The massive material from Kalgoorlie is pale bronze-yellow with bright metallic lustre; and with its sub-conchoidal fracture and absence of cleavage it much resembles iron-pyrites in appearance—in fact, before its value was recognised, the mineral had been thrown away on the waste heaps of the mines. L. J. S.

CALCIDINE. Calcium iodide.

CALCINOL. Calcium iodate.

CALCITE or **CALC-SPAR.** One of the dimorphous crystallised forms of calcium carbonate ($CaCO_3$). This rhombohedral form is less dense (sp.gr. 2·72) and less hard (H. 3) than the orthorhombic form aragonite (*q.v.*). It is also the more stable form: when aragonite is heated to low redness it passes into calcite, and paramorphs of calcite after aragonite are of frequent occurrence in nature. From an aqueous solution containing carbon dioxide, calcium carbonate crystallises as calcite at temperatures of 0°–[illegible]°, and as a mixture of calcite and aragonite at higher temperatures: the presence of various salts in the solution also favours the formation of aragonite. (For a summary of the literature on the crystallisation of calcium carbonate, *see* F. Vetter, Zeitsch. Kryst. 1910, xlviii. 45.) Calcite may be readily distinguished from aragonite by the possession of three perfect cleavages parallel to the faces of the primary rhombohedron, the angles between which are 74° 55′ and 105° 5′ (the plane angles on the rhomb-shaped faces are 78° and 102°). The mineral is readily scratched with a knife, and it effervesces briskly in contact with cold dilute acids.

With the exception of quartz, calcite is the commonest of minerals. It frequently occurs well crystallised and in a great variety of forms, the various forms of its crystals suggesting the trivial names 'dog-tooth-spar,' 'nail-head-spar,' 'paper-spar,' 'cannon-spar,' &c. As the essential constituent of the rocks limestone, marble, and chalk, it is of abundant occurrence. In these forms it finds extensive applications as building and ornamental stones, and in the manufacture of lime, mortar, and cement. The clear, transparent variety, known as Iceland-spar or doubly-refracting spar, is used in the construction of nicol prisms for optical polarising apparatus. Material suitable for this purpose is obtained almost exclusively from a quarry in basalt on the Reydar-fjördhr on the east coast of Iceland, but the supply is limited and variable.

A considerable quantity of clear material suitable for optical work has been found (1918) between Greycliff and Bigtimber in Montana, where it occurs in vertical veins in gneiss

L. J. S

CALCIUM. Symbol Ca. At. wt. 40·0. Lime, the oxide of calcium, has been employed in the preparation of mortar from very early times. Interesting accounts of the process of lime-burning are given by Dioscorides and Pliny. It was not, however, until 1756 that the difference between burnt and unburnt lime was explained by Black.

Calcium is universally found as carbonate $CaCO_3$ in the forms of *calcspar*, *marble*, and *limestone*, often in whole mountain ranges or immense coral reefs. *Dolomite* or *bitter spar*, the double carbonate of calcium and magnesium, constitutes the geological formation termed magnesian limestone. Calcium sulphate as *anhydrite* $CaSO_4$ or *selenite* (*gypsum*) $CaSO_4+2H_2O$, is also very plentiful. The phosphate united with the chloride or fluoride also occurs widely distributed, often as minute inclosures in crystals of the primary rocks, as the mineral *apatite*, whilst calcium is an important base in the greater number of natural silicates. The soluble matter carried away by rivers largely consists of the carbonate and sulphate of calcium, while sea-water contains, in addition to these, both phosphate and fluoride of calcium. The bones of animals consist largely of calcium phosphate, and the shells of molluscs of the carbonate. Calcium salts are never absent from plant tissues, concentrating mainly in the leaves.

Calcium also occurs in extra-terrestrial bodies, in the sun, meteorites, and many fixed stars.

Preparation of the metal.—Calcium was obtained as an impure metallic powder by Davy in 1808, by the electrolysis of the chloride, using mercury as negative electrode, and afterwards heating the amalgam thus formed until the mercury was volatilised. It was obtained as a metallic solid by Matthiessen in 1856 (Chem. Soc. Trans. 8, 28), by electrolysing a fused mixture of calcium and strontium chlorides in the proportion of two molecules to one with a little ammonium chloride, the whole being contained in a porcelain crucible. On passing the current, beads of metallic calcium separated at the negative pole and were ladled out. Moissan (Ann. Chim. Phys. [7] 18, 289) repeated the experiment, increasing the size of the apparatus, and obtained a metal possessing a yellowish colour.

Lies-Bodart and Gobin (Compt. rend. 47, 23) obtained calcium by heating the iodide with an equivalent of sodium in an iron crucible, the lid of which was screwed down. Moissan repeated the experiment several times, and states that the yield and purity vary greatly, the richest metal obtained containing from 83 p.c. to 93 p.c. calcium. The reaction proceeds best at a dull red heat, and is reversible if afterwards the temperature is raised to whiteness.

Frei obtained calcium in globules weighing 2·4 to 4 grams by the electrolysis of the chloride.

Another process consists in fusing 3 parts of calcium chloride with 4 parts of zinc and 1 part of sodium, thus forming an alloy of zinc and calcium, which, when heated in a gas-carbon crucible, decomposes, the zinc volatilising and a button of fused calcium remaining (Caron, Annalen, 115, 355).

Moissan obtained the alloy with facility, but was unable to separate the calcium from it.

Moissan (*l.c.*) points out that in all the above methods the difficulty is to free the calcium from the metal with which it has become associated in the preparation. He, however, finally succeeded in obtaining the pure metal by utilising the property, unknown before his researches, of molten sodium to dissolve calcium. For the preparation, he adopted a modification of the method of Lies-Bodart and Gobin. In an iron crucible of about 1 litre capacity he placed a mixture of 600 grams of coarsely crushed anhydrous calcium iodide, with 240 grams of sodium in pieces as large as nuts. The crucible was closed with a screw lid and maintained for 1 hour at a dull-red heat, then allowed to cool. The calcium, which is soluble in excess of sodium at a red heat, separates at the point of solidification and becomes practically insoluble. The metallic portion of the melt is cut up into medium-sized fragments and gradually introduced into absolute alcohol. The sodium dissolves, leaving the calcium in brilliant white crystals, 98·9 p.c. to 99·2 p.c. pure.

Ruff and Plato have succeeded in obtaining the metal in relatively large quantities by the electrolysis of fused calcium chloride by keeping the temperature of the cathode above the melting-point of calcium (U.S. Pat. 806006). Borchers and Stockhem, by electrolysing fused anhydrous calcium salts, keeping the temperature of the cathode below the melting-point of calcium, obtained the metal in a spongy state (U.S. Pat. 808066). By using a vertical cathode, which only just touches the surface of the fused calcium salt, the metal is deposited on this surface, and by mechanically raising the cathode an irregularly shaped rod of calcium, resembling a cabbage stalk, is formed, which itself forms the cathode (Eng. Pat. 20655; *cf.*

Johnson, J. Ind. Eng. Chem. 1910, 2, 466). The electrolyte consisting of a fused mixture of 10 parts of $CaCl_2$ with 17 parts of CaF_2, is contained in a cylindrical vessel of Acheson graphite. The containing vessel forms the anode, whilst the cathode is an iron ribbon which can be run up from below. The best deposits were obtained with a current density of 10 ampères per square cm. If the cathode current density is too high the metal does not adhere, whilst if the anode density is too low the eletrolyte is not all melted, and for proper control the anode and cathode surfaces should be definite for the conditions in use. Maldenhauer and Andersen (Zeitsch. Elektrochem. 19, 144) used a mixture of 85 p.c. $CaCl_2$ with 15 p.c. KCl and a current density of 60-110 ampères per square cm. Rods 9–18 mm. diameter were obtained, containing Ca 96·09–98·18, K 0·0–0·14, Fe 0·3–0·4, Si 0·40–0·70. The current yield varied from 65 to over 90 p.c.

Commercial calcium is usually coated with $CaCl_2$, which can be partly removed by absolute alcohol, and the remainder by re melting in an iron bomb. In this way a metal containing 99·44 p.c. Ca and 0·25 $Al_2O_3 + SiO_2$ is obtained.

Calcium is made commercially at Bitterfeld, Germany. The world's production is about 50 tons a year, and the price in normal times is about 12*s.* 6*d.* a pound. The metal melts at 810°, and has a density of 1·548. It may be turned into cylinders having a brilliant lustre tarnishing in air. It may be drawn into wire of 0·5 mm. diameter. Its electric conductivity is 16, that of silver being 100.

Calcium is a white metal approaching silver in colour. It can be cut with a knife or broken with a blow, and the fracture is crystalline. It scratches lead, but not calcite. It is less malleable than sodium or potassium. The crystals are of tabular habit and belong to the rhombohedral system.

Gently heated in air, it burns with incandescence, or if heated in a current of air at a dull-red heat it leaves a spongy mass which decomposes water, producing ammonia and calcium hydroxide. Calcium, therefore, fixes both nitrogen and oxygen. Calcium inflames when heated in oxygen to 300°, and the heat is so great that the lime formed is both fused and partly volatilised. Fluorine gas violently attacks calcium at the ordinary temperature. Chlorine, bromine, and iodine have no action until heated to 400° or above. Metallic calcium exists in both an active and an inactive form in its power of absorbing gases. Active calcium commences to absorb nitrogen at 300°, and has a maximum action at 440°. As the temperature increases the rate of combination slowly decreases, until at 800° it has ceased. The velocity of absorption is dependent on the presence of a layer of nitride. The inactive form commences to combine with nitrogen at 800°. The difference is not due to the existence of allotropes, but to the state of sub-division. The active variety is prepared by slowly cooling molten calcium. This variety produces a black nitride (Zeitsch. Elektrochem. 22, 15). Water is attacked at the ordinary temperature with the liberation of hydrogen; the action is slow, owing to the formation of a crust of calcium hydroxide; the addition of sugar hastens the action. Fuming nitric acid attacks it only slowly if free from lime; the action is hastened on dilution. Fuming sulphuric acid is immediately reduced in the cold to sulphur and sulphur dioxide. Hydrochloric and acetic acids attack calcium violently, with the liberation of hydrogen. At a red heat, calcium reduces the fluorides and chlorides of potassium and sodium, setting free the alkali metals; under the same conditions, the iodides are not attacked.

Calcium, although soluble in molten sodium, from which it separates in the crystalline state on solidification of the solvent, is not notably soluble in potassium. The only definite compound with mercury appears to be $CaHg_4$, m.p. 266° (decomp.). With magnesium, it furnishes an alloy which decomposes cold water. The freezing-point curve has a simple form, the single compound Ca_3Mg_4 being indicated by a maximum at 715°, whilst there are eutectic points at 514° and 446° and 18·7 and 78·7 p.c. of Ca respectively. The compound Ca_3Mg_4 is brittle, silvery in appearance, stable in air, and is only slowly acted on by water. Lead and calcium react together violently in the molten state; the freezing-point curve has maxima at 649° and 1105°, corresponding with the compounds $CaPb_3$ and Ca_2Pb respectively. Another compound CaPb is formed at 950°. All the alloys fall to a black powder in air. Copper and calcium form a single compound $CaCu_4$, melting at 933°, unstable in air. Silver and calcium form a complicated system of alloys (Zeitsch. Anorg. Chem. 70, 352. With zinc and nickel it forms brittle alloys. Tin, heated just above its point of fusion, combines with it with incandescence, forming a white crystalline alloy, containing 3·82 p.c. calcium.

Calcium hydride. CaH_2. Calcium does not unite with hydrogen at the ordinary temperatures. To prepare it, the metal cut into small pieces contained in several nickel boats, is placed in a glass tube sealed at one end. Hydrogen is fed in at a pressure of 4 to 5 cms. mercury, the tube being heated to redness; the temperature is kept sufficiently low to prevent union between the calcium and the nickel. So obtained, it is a fused white solid; sp.gr. 1·7. It may be heated to redness in air without change. Its characteristic reaction is the decomposition of water in the cold with the liberation of hydrogen. Calcium hydride shows a marked dissociation from 600°, reaching one atmosphere pressure below 800°. This cannot be a true dissociation pressure, as the hydride is readily formed by heating calcium in hydrogen at 830°. A second hydride also exists

$$Ca+H \rightarrow CaH+23{,}100 \text{ cal.}; \quad CaH+H \rightarrow CaH_2+22{,}000 \text{ cal.}$$

(Zeitsch. Electrochem. 20, 81). Brönsted calculates the heat of formation of calcium hydride from solution in hydrochloric acid: for CaH from liquid calcium and hydrogen about 21,000, and for CaH_2 from CaH and hydrogen 21,000. Gunts and Barrett found 46,200 cal. from solid calcium (Zeitsch. anorg. Chem. 82, 130). A mixture of $BaSO_4$ and CaH_2 ignited by a fuse similar to that used in thermite react vigorously according to the equation:

$$BaSO_4+CaH_2=BaS+4CaO+4H_2$$

(Ber. 46, 2264).

Calcium oxide, Lime. CaO. Anhydrous

Calcium oxide (quicklime) is obtained by heating to redness any salt of calcium containing a volatile acid, as the carbonate and nitrate. Calcium carbonate, when heated in a closed vessel, may be fused without decomposition, but when raised to a red heat under ordinary pressure it gives off its carbon dioxide, and becomes converted into lime $CaCO_3 = CaO + CO_2$

To obtain pure lime, Iceland spar or other forms of calcite, or the finest marble, may be employed, the ignition being performed in a crucible with perforated base so as to permit of the entrance of furnace gases, which carry away the carbon dioxide as fast as it is formed; otherwise the decomposition is incomplete, the carbonate undergoing no change in an atmosphere of carbon dioxide.

Lime is made by heating calcium carbonate to a temperature high enough to drive off the carbonic acid. The tension of dissociation of $CaCO_3$ is 27 mm. at 547° and 753 mm. at 812°; in practice, the temperature for burning lime is about 1000°. The raw material may be nearly pure calcium carbonate such as marble or chalk, or may contain so much clayey matter that the product is a cement of the Portland class rather than a lime. On this fact choice of the mode of burning in part depends, because if the lime is needed to be pure it must be burnt out of contact with solid fuel, whereas if it is a cement rather than a lime, the addition of silicious matter from the ash of the fuel may be actually an advantage. The chief uses of lime are for building, in agriculture and for chemical manufacture. For the first purpose an impure limestone, burnt in contact with solid fuel, is to be preferred, whereas the purest obtainable limestone, heated out of contact with fuel, yields the best material for chemical use. In practice these [illegible] rules are not always observed, partly from [illegible] validity and partly [illegible] economical to sacrifice the purity of the product rather than incur the expense in capital and fuel of kilns designed to burn limestone out of contact with solid fuel, but the knowledge of these is of value in deciding on the type of kiln to be adopted in any given case.

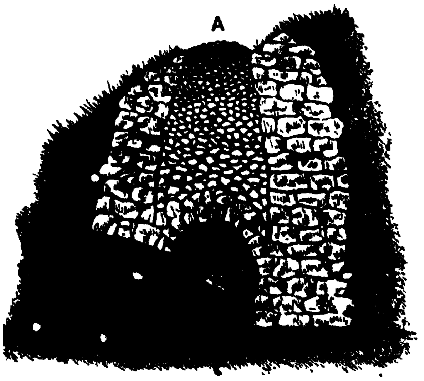


FIG. 1.

The simplest form of kiln is the flare kiln, shown in Fig. 1. The fuel (wood or peat) is burnt under an arch made of the material to be calcined, thus [illegible]duced is uncontaminated with ash [illegible] a device is, of course, not economical of fuel, but its simplicity and cheapness, and the fact that it can produce excellent lime, cause it to be still used to a considerable extent.

Another simple form is the common running kiln shown in Fig. 2. The limestone or chalk is loaded into the kiln with alternate layers of small coal or coke, and the product is from time to time drawn from an eye at the bottom of the kiln, fresh layers of raw material and fuel being added through the charging hole at the top of the kiln. Lime made in kiln of this class, of course, contains the whole of the ash of the fuel.

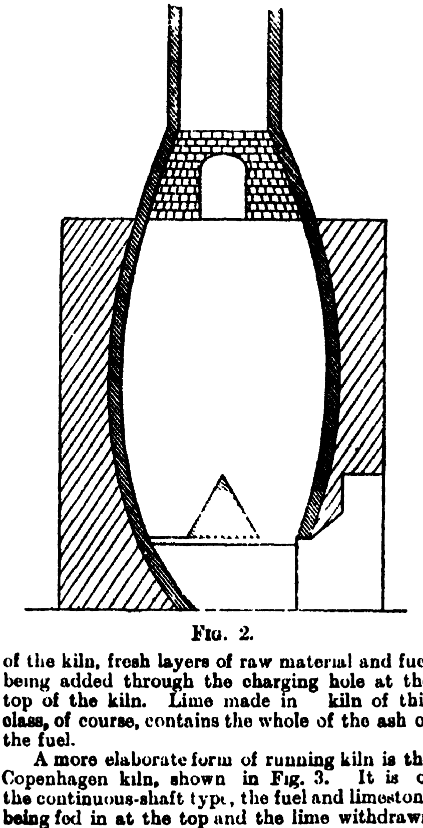


FIG. 2.

A more elaborate form of running kiln is the Copenhagen kiln, shown in Fig. 3. It is of the continuous-shaft type, the fuel and limestone being fed in at the top and the lime withdrawn at the bottom, but in addition a definite burning zone is established by feeding a portion of the fuel in at the side openings giving into the central part of the kiln. The heat can thus be controlled better than when all the fuel is distributed through the whole of the charge, with the result that consumption of fuel is decreased.

Another shaft kiln is the Ryan kiln, used in the Buxton district. Its construction is shown in Fig. 4. The fuel is fed in at the sides and the limestone at the top, so that the ash of the former is less inextricably mixed with the burnt lime. In consequence and because of the hardness and dense structure of Buxton limestone, a large part of the output is in lump practically uncontaminated with ash, so that the product can be picked and the lump of lime of high purity sold for chemical use, such as the manufacture of bleaching powder.

Lime can be burnt in a rotatory kiln, similar to those used for cement but worked at a lower temperature, but few such kilns are in use, the probable reason being that only small lime would be produced, and for many uses lump lime is preferred.

The Hoffmann kiln (Fig. 5) is used in places where labour is sufficiently cheap to allow of loading and unloading by hand being performed at a low cost; it has the advantage of being economical of fuel. The burning chamber consists of an endless tunnel, divided into compartments of approximately equal size by means of combustible dampers. Each chamber is [illegible] an opening in the [illegible] and discharging. [illegible] connecting with the [illegible] fuel of breeze and coal is introduced [illegible] holes in the arched roof. The kiln [illegible] scheme, fuel being charged [illegible] chamber, and air being allowed to [illegible] complete the calcination while [illegible] damper [illegible] production of these [illegible] large.

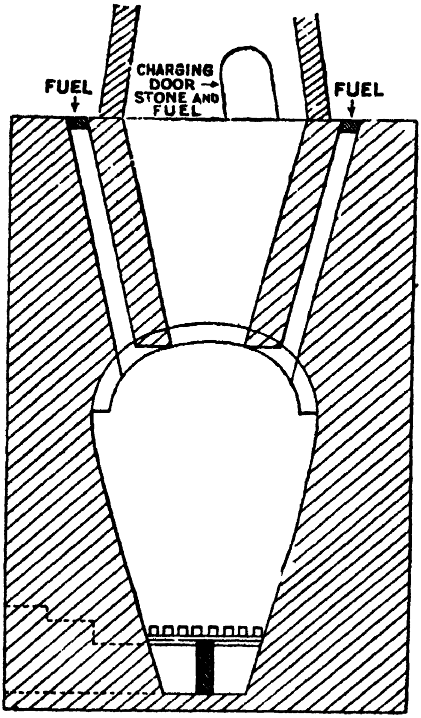


FIG. 3.—COPENHAGEN KILN.

Passing from those kilns [illegible] except the flare kiln, which allow at least some contact of the ash of the fuel with the lime, to gas fired kilns in which contact is wholly avoided, an intermediate type is the Rumford kiln, shown in Fig. 6.

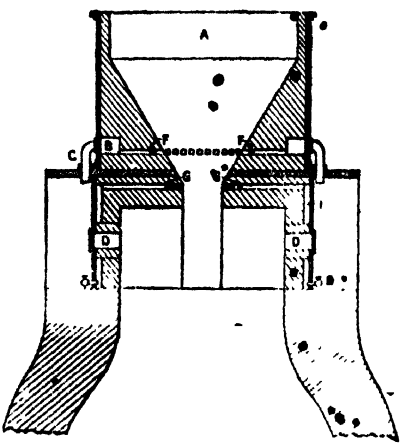


FIG. 4

The fuel is burnt on the hearth of a furnace beneath a bridge up through which the gaseous products of combustion pass to the shaft of the kiln and over which descends the burnt lime to openings at the side where it can be drawn.

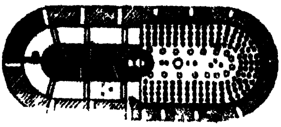


FIG. 5.

A gas-fired kiln proper is the Schmatolla kiln, shown in Fig. 7. Gas, from a producer at the side of the kiln, flows through ports in the walls of the kiln shaft, and there burns with a supply of secondary [illegible] heated [illegible] through the hot lime which has descended below the level [illegible] gas inl[illegible] of [illegible] fuel [illegible] ash [illegible] [illegible] almost entirely [illegible] material closely [illegible] The following an[illegible]

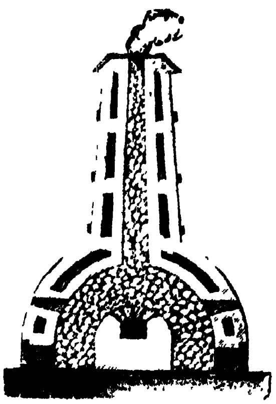


FIG. 6.

from [illegible] to a

	Buxton lime	Common building lime	Chaux de Teil	Blue Lias lime
Insoluble residue	0 71	18·20	0·62	2·39
Combined silica (SiO_2)		10·34	22·10	14·17
Alumina (Al_2O_3)	0·11	1·64	1 82	6·79
Ferric oxide (Fe_2O_3)				2·34
Lime (CaO)	98·72	51·10	66·72	63·43
Magnesia (MgO)	0·46	1·04	1·17	1·54
Sulphuric anhydride (SO_3)	—	0·21	0·49	1·63
Carbonic anhydride (CO_2)	—	8·00	0·64	3·64
Water (H_2O)	—	14·47	5·36	2·69
Alkalies and loss	—		1·08	1·38
	100 00	100 00	100 00	100 00

As mentioned above, the purest kinds are needed for chemical manufacture, and the less pure varieties which approach the nature of cement, are generally preferable for building. In the case of limes containing so much silica as does Chaux de Teil and so much silica and alumina as does Blue Lias lime, they may be regarded as hydraulic cements rather than limes proper. A rough trade distinction exists between 'fat' and 'poor' lime. The former is fairly pure and slakes rapidly and with a high rise of temperature; the latter, containing some combined silica and alumina, slakes slowly and relatively feebly. Both, when mixed with sand form mortars, but fat lime sets only [illegible] and subsequent absorption of [illegible] acid from the air, whereas the silicious constituents in poor lime will themselves set, to some small extent, in the manner of a cement. Pure lime, mixed with pure quartz sand, has no appreciable action on it at the ordinary temperature, but may act in slight degree on the more attackable silicious concomitants of common building sand; in any case, however, the action is trifling, and the setting of common mortar is practically unaffected by any such occurrence. In building, therefore, where an hydraulic cement is not necessary, a moderately silicious lime, which will set lightly *per se*, is preferable to the fat lime commonly employed. In this country, lime is almost always slaked on the spot and at the time where it is to be used. Abroad, the lime is usually slaked long before it is used, and is thus allowed to become completely hydrated. The easiest plan is to make a paste of lime and water (lime putty), and keep it in a pit until it is needed. In like manner, slightly hydraulic lime is slaked with a limited quantity of water and allowed to remain in silos until the lime itself is completely hydrated, whilst the cementitious silicates remain unaffected and ready to act as cement when the lime is put to use.

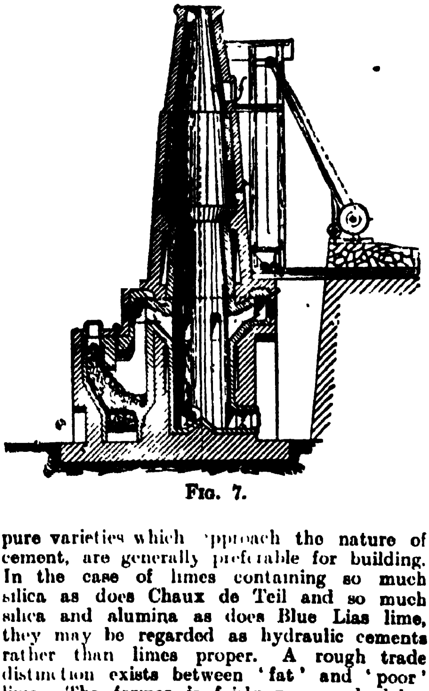


Fig. 7.

When a dolomitic limestone is burnt, it yields a lime of which the following is an example:—

	Per cent
Insoluble silicious matter	2·94
Alumina + ferric oxide ($Al_2O_3 + Fe_2O_3$)	1·90
Lime (CaO)	46·72
Magnesia (MgO)	32 60
Sulphuric anhydride (SO_3)	0·92
Carbonic anhydride (CO_2)	3·27
Combined water and loss	11·65
	100·00

Lime of this kind needs much care in slaking, as the hydration of the magnesia takes place slowly and may occur after the mortar is in place, and by expansion cause destruction of the work.

Although lime will not act on sand at the ordinary temperature, yet, like other alkaline bodies it attacks it readily at a moderate temperature. The manufacture of sand lime bricks is dependent on this fact. The bricks of sand, mixed with 5–10 p.c. of lime just hard enough to stick together, are exposed to steam at about 150°; at that temperature the lime acts on the sand, producing calcium silicates, which are cementitious, and suffice to cement the sand grains together into a brick of ample strength for ordinary building purposes. In places where sand is abundant and clay suitable for brick making is scarce, the process is of considerable use.

Pure calcium oxide forms white porous amorphous masses of sp.gr. 2·3 to 3·08, highly infusible, melting only in the highest temperature of the oxyhydrogen blowpipe flame or in the electric arc. In the ordinary oxyhydrogen flame it emits an intense light, which is much used for lantern projection.

Calcium oxide has been obtained by Brügelmann in minute cubic crystals of sp.gr. 3·251 by heating the nitrate in a porcelain flask (Pogg. Ann. [2] 2, 466; and [2] 4, 277).

A crystalline mass, found upon the lining of a continuous limekiln at Champigny after 28 months' continuous work, was also shown to consist of small cubical crystals of pure lime, of sp.gr. 3 32 (Levallois and Meunier, Compt. rend. 90, 1566).

There is evidence of the existence of two forms of calcium oxide. The oxide obtained by heating calcite at a low red heat is fine grained and porous. When heated at higher temperatures the refractive index increases and cubic crystalline calcium oxide is formed for which $N_D = 1·83$. The melting-point of CaO as determined by the Holborn Kurlbaum optical pyrometer is 2570° (J. Washington [illegible] 133, 315).

Amorphous lime takes up water [illegible] markable avidity, forming calcium hydroxide $Ca(OH)_2$, the combination being accompanied by a contraction in volume and evolution of heat. Owing to this property, it is used extensively in the laboratory and works as a drying agent. On exposure to air, the amorphous variety of lime rapidly absorbs water and carbon dioxide; anhydrous lime, however, only absorbs the gas when heated to near 415°. Comparative tests show that carbon dioxide penetrates to a depth of about 3 inches in 20 days. More water is taken up in summer than in winter, but the carbon dioxide absorption is about the same (Whetzel, J. Ind. Eng. Chem. 1917, 7. 287) Lime is readily soluble in dilute mineral acids. It also reacts with ethyl alcohol when heated in a sealed tube to 115° to 125°, giving a mixture of hydrate and ethylate of calcium.

Calcium hydroxide, or Hydrate of lime, $Ca(OH)_2$, is obtained by slaking fresh well-burnt quicklime with about a third of its weight of water. It forms a white amorphous powder of sp.gr. 2·078, sparingly soluble in water, and less so in hot than in cold water, as seen from the following table (Maben, Pharm. J. [3] 14, 505):—

Temperature	Parts of water required to dissolve one part CaO	Temperature	Parts of water required to dissolve one part CaO
0°	759	55°	1104
5°	764	60°	1136
10°	770	65°	1208
15°	779	70°	1235
20°	791	75°	1313
25°	831	80°	1362
30°	862	85°	1388
35°	909	90°	1579
40°	932	95°	1650
45°	985	99°	1650
50°	1019		

According to Lamy (Compt. rend. 86, 333), the solubility varies slightly with the method of preparation of the hydroxide.

The solution known as lime water has an alkaline reaction, and absorbs the carbon dioxide of the atmosphere, forming a pellicle of calcium carbonate. Lime water of definite strength for pharmaceutical purposes, is best prepared by using freshly ignited lime. In preparing lime water from ordinary lime, the first solutions should invariably be rejected, as they will contain nearly all the soluble salts of the alkalis and the baryta and strontia present in the lime as impurities. Milk of lime is an emulsion of calcium hydroxide suspended in less water than is required for its complete solution. Calcium hydroxide is much more soluble in solution of sugar than in pure water, due to the formation of soluble saccharates (for solubilities, *v.* Weisberg, Bull. Soc. chim. 21, 773).

Calcium hydroxide is precipitated by caustic potash or soda from strong solutions of the chloride; if a saturated solution of calcium chloride be employed, the whole becomes solid.

A solution evaporated over sulphuric acid in a vacuum deposits hexagonal prisms, according to Gay-Lussac. Crystals, however, which had separated on the surface of samples of hydraulic cement were found by Glinka to belong to the rhombic system in spite of their hexagonal appearance. A deposit of grey lamellæ, consisting of calcium hydroxide, was found by Luedecke in a Carré ice machine. Selivanov (J. Russ. Phys. Chem. Soc. 45, 252) finds that supersaturated solutions of hydrated calcium oxide contain 0·260 to 0·264 gram CaO per 100 c.c. These saturated solutions are extremely sensitive to heat. The monohydrate $Ca(OH)_2$ may be obtained in hexagonal plates by heating the solution. The cryohydrate gives on solidification transparent ice, but the solution formed when the ice melts deposits the sesqui-hydrate $2Ca(OH)_2,H_2O$ in elongated hexagonal or rhombic plates. The compound is very unstable.

Calcium hydroxide is an energetic base combining with acids to form salts and displacing ammonia from its compounds.

At a red heat, calcium hydroxide is decomposed, water being driven off and oxide remaining.

Slaked lime is used extensively in the preparation of mortars and cements (*v.* CEMENTS), for softening hard water, in the preparation of lyes and defecation of sugar, and for agricultural purposes. It has been noted that as regards the application of lime to the soil, only a small proportion reappears as carbonate, the remainder being adsorbed by the soil constituents.

Calcium dioxide CaO_2 was first prepared by Thenard by the action of excess of hydrogen peroxide upon lime-water, when microscopic quadratic plates of the composition $CaO_2.8H_2O$, sparingly soluble in water and insoluble in alcohol, were precipitated. According to Conroy (Chem. Soc. Trans. 1873, 810), the peroxide is most conveniently prepared by adding lime-water in considerable excess to an aqueous solution of sodium peroxide acidulated with nitric acid. It is also obtained, as a finely divided white precipitate on adding a neutral or alkaline solution of sodium peroxide to a solution of a calcium salt. The crystals are isomorphous with those of hydrated barium peroxide. On exposure to air they effloresce, and when heated to 130° are converted into the anhydrous peroxide. On increasing the heat, half the oxygen is driven off, leaving a residue of pure lime. CaO_2 in the anhydrous form (Riesenfeld and Nottebohm, Zeitsch. anorg. Chem. 89, 405) separates from very concentrated solutions near 0°, and above 40° even from very dilute solutions. The octahydrate is obtained from very dilute solutions at the ordinary temperature. The octahydrate is dehydrated at 100° There is no appreciable decomposition below 200°. Up to 273° decomposition is slow, but then becomes very rapid. Finely divided CaO_2 decomposes explosively when heated rapidly to 275°. The dissociation pressure at 255° is more than 190 atmospheres.

Calcium chloride $CaCl_2$ is found in the water of nearly all springs and rivers, and is consequently a constituent of the saline matter dissolved in sea-water. This salt also forms the chief saline constituent of an exudation occurring on the face of the old red sandstone rocks at Guy's Cliff, in Warwickshire, occurring to the extent of 27·15 p.c. (Spiller, Chem. Soc. Trans. 1876, 1, 154). Calcium chloride likewise occurs, together with magnesium chloride and alkaline chlorides in the *tachydrite* and *carnallite* of the Stassfurt deposits, *tachydrite* containing 21 p.c. $CaCl_2$ and 36 p.c. $MgCl_2$, while *carnallite* contains 3 p.c. $CaCl_2$, and 31 p.c. $MgCl_2$.

Calcium chloride may be obtained by passing chlorine over the red-hot oxide, or by dissolving lime, chalk, or marble in hydrochloric acid and evaporating. If it is necessary to obtain the salt pure, chlorine water may be added to the solution in hydrochloric acid in order to oxidise any iron present, which may then be precipitated by the addition of milk of lime, and filtered off. The slightly alkaline filtrate is then acidified with hydrochloric acid and evaporated to the crystallising point.

Calcium chloride is obtained in large quantities as a by-product in many manufacturing processes, notably in the preparation of potassium chlorate and in the manufacture of sodium carbonate by the ammonia-soda process; it may be obtained in the pure state from these crude products by the method just indicated. Many attempts have been made to utilise this waste calcium chloride. Richardson (E. P. 10418) treats the purified crude solution with ammonium sulphate in the proportion required to convert all the chloride into sulphate; the calcium sulphate could then be filtered off, and ammonium chloride recovered by crystallisation. Pelouze (Compt. rend. 52, 1267) was the first to point out that calcium chloride mixed with sand to prevent fusion is almost completely decomposed when heated to redness and treated with steam, the chlorine being evolved as hydrochloric acid. The process was patented by Solvay, and the method applied to the waste calcium chloride liquors, but the condensed hydrochloric acid obtained is dilute and does not pay for the coal consumed in the operation. Lunge considers that so long as hydrochloric acid is so cheap, no possible method can be found to utilise the chlorine in the waste liquors at a profit.

Saturated solutions of calcium chloride deposit the hydrated salt in large hexagonal prisms terminated by pyramids, of the composition $CaCl_2,6H_2O$. The crystals melt at 29° in their water of crystallisation and deliquesce rapidly in the air, forming a viscous fluid, formerly termed *oleum calcis*. Heated below 200°, or in a vacuum over sulphuric acid, the crystals lose four molecules of water. The remaining two molecules can only be expelled above 200°. According to Weber (Ber. 15, 2316), the salt dried at 180°-200° is practically anhydrous, containing only 0·2 p.c. of water. Besides the two hydrates above described, Lescœur (Compt. rend. 92, 1158), from determinations of maximum tensions of solutions, shows the probable existence of two others $CaCl_2,4H_2O$ and $CaCl_2,H_2O$. The tetrahydrate, however, can only exist below 129°. Milikan (Zeitsch. physikal. Chem. 92, 496) has examined the equilibrium conditions in the system $CaCl_2-HCl-H_2O$. The solution containing 44·5 p.c. $CaCl_2$ and 3·3 p.c. HCl is in equilibrium with the solid phases $CaCl_2,6H_2O$ and $CaCl_2,4H_2O$ and the solution containing 28·48 p.c. $CaCl_2$ and 21·40 p.c. HCl with the solid phases $CaCl_2,4H_2O$ and $CaCl_2,2H_2O$.

Anhydrous calcium chloride is a white porous mass, which fuses at a red heat or, according to Le Chatelier (Bull. Soc. chim. 47, 300), at 755°. On cooling, the salt solidifies to a translucent mass of crystals of sp.gr. 2·205. A slight decomposition into oxide and carbonate occurs when the fusion is performed in air. On this account, the porous chloride obtained by drying the crystals at 260° is better adapted for desiccating purposes, especially for the absorption of water in organic analysis. McPherson (J. Amer. Chem. Soc. 1917, 39, 1317) has shown that granular calcium chloride when absolutely dry will remove every trace of moisture from a gas passed over a sufficiently long column of it. If the fused mass is exposed to the sun's rays, it becomes phosphorescent in the dark, and was formerly called *Homberg's phosphorus*, after the discoverer of the fact in 1693.

Anhydrous calcium chloride is highly deliquescent. 100 parts of the powder exposed to an atmosphere saturated with aqueous vapour absorb 124 parts of water in 96 days. According to Kremers (Pogg. Ann. 103, 57; 104, 133; J. 1858, 40), the following quantities of water are required to dissolve one part by weight of the anhydrous salt:—

At 10·2°	20°	40°	60°
1·58	1·35	0·83	0·72

In the following table, drawn up by the same author, are shown the specific gravities of solutions of varying strengths:—

Quantities in 100 parts water	Sp.gr. of solutions at 19·5° (water at 19·5°=1)
6·97	1·0545
12·58	1·0954
23·33	1·1681
36·33	1·2469
50·67	1·3234
62·90	1·3806

According to Engel (Bull. Soc. chim. 47, 318), 100 parts of water at 0° dissolve 60·3 parts $CaCl_2$, forming a solution of sp.gr. 1·367.

A solution of 50 parts anhydrous $CaCl_2$ in 100 parts water, boils at 112°, one containing 200 p.c. boils at 158°, and a 325 p.c. solution boils at 180°.

According to Lefebvre (Compt. rend. 70, 684) a supersaturated solution of calcium chloride is formed by dissolving 350–400 grams of the crystallised salt in 50 c.c. warm water or 200 grams of the anhydrous salt in 250 c.c. water; it may be shaken after cooling without crystallisation, but solidifies on contact with a crystal of the salt. If cooled to 5·8°, this solution begins to crystallise, the temperature rising to 28°–29°. A solution containing 55 p.c. $CaCl_2$ deposits at about 15° large plates of the tetrahydrate $CaCl_2,4H_2O$, which do not induce the crystallisation of the supernatant liquor. This solution, in passing from liquid to solid state, undergoes at 70° a contraction 0·0832 of its volume.

The crystallised chloride $CaCl_2,6H_2O$ also deliquesces rapidly, and dissolves in half its weight of water at 0°, in one-fourth its weight at 16°, and in all proportions of hot water. In dissolving it absorbs heat, while the anhydrous chloride dissolves with evolution of heat. A mixture of 1·44 parts crystallised chloride with 1 part of snow produces a cold of −54·9°, more than sufficient to freeze mercury.

Both the anhydrous and hydrated chloride dissolve readily in alcohol, 10 parts at 80° dissolving 6 parts anhydrous $CaCl_2$; on evaporation in a vacuum at winter temperature, rectangular plates of $2CaCl_2,7C_2H_6O$ are deposited.

Anhydrous calcium chloride absorbs ammonia gas, forming the compound $CaCl_2,8NH_3$ as a white powder, which, on exposure to air, solution in water, or on heating, is decomposed. Thrown into chlorine gas, the compound takes fire. Calcium and barium chlorides form the double salt $CaCl_2,BaCl_2$ (m.p. 631°), but no mixed crystals. Calcium and strontium chlorides form a continuous series of mixed crystals with a minimum melting-point at 658° and 60 mol. p.c. $CaCl_2$ (Jahr. Min. 15).

Calcium oxychloride. When calcium chloride solution is boiled with slaked lime, and the liquid filtered, white needle-shaped crystals of calcium oxychloride separate out on cooling of the composition $ClCa{\cdot}O{\cdot}Ca(OH),7H_2O$ or $3CaO{\cdot}CaCl_2,15H_2O$ (Grimshaw, Chem. News, 30, 280). The salt is stable out of contact with air, loses part of its water of crystallisation over sulphuric acid or caustic lime, and absorbs carbon dioxide from the atmosphere. It is decomposed by water or alcohol.

According to André (Compt. rend. 92, 1452), the composition of the salt is

$$CaCl_2{\cdot}3CaO,16H_2O$$

and, on drying in a vacuum, it becomes converted into $CaCl_2{\cdot}3CaO,3H_2O$.

When calcium chloride is fused at a bright-red heat in a current of moist air, it is gradually converted to an oxychloride of the composition $CaCl_2{\cdot}CaO$, and eventually to oxide (Gorgeu, Compt. rend. 99, 256).

Calcium hypochlorite v. BLEACHING POWDER.

Calcium chlorate $Ca(ClO_3)_2$ is produced when chlorine is passed into hot milk of lime, but is difficult to separate from the chloride simultaneously formed. This is the first step in the manufacture of potassium chlorate, and the reaction is supposed to be as follows:—

$$6Ca(OH)_2+6Cl_2=Ca(ClO_3)_2+5CaCl_2+6H_2O.$$

According to Lunge (J. Soc. Chem. Ind. 1885, 722), the reaction really takes place in several stages, calcium hypochlorite and hypochlorous acid being first formed and mutually reacting with production of calcium chlorate:

(1) $Ca(OCl)_2+4Cl+2H_2O=CaCl_2+4HClO.$
(2) $2Ca(OCl)_2+4HClO=CaCl_2+Ca(ClO_3)_2+4Cl+2H_2O.$

The free chlorine serves only as carrier of the oxygen of two molecules calcium hypochlorite to a third molecule of the hypochlorite which is oxidised to chlorate. Lunge's experiments show that the best mode of converting hypochlorite into chlorate is to raise the temperature of the solution, slight excess chlorine being at the same time present. The heat produced by the reaction on the large scale is sufficient.

Calcium chlorate can best be prepared by the electrolysis of a 10 p.c. solution of calcium chloride. The density of the current should be 10 amperes per square decimeter at the anode and double at the cathode; temperature 50° (Zeitsch Elektrochem. 4, 464).

It may also be prepared by precipitating potassium chlorate with calcium silicofluoride. It crystallises in deliquescent rhomboidal plates, very soluble in water and alcohol; the crystals contain 16·5 p.c. water, melt when warmed, and decompose on further heating.

Calcium perchlorate $Ca(ClO_4)_2$ may be obtained by saturating perchloric acid with caustic lime. It is extremely deliquescent and crystallises in prisms soluble in alcohol.

Calcium bromide $CaBr_2$ (m.p. 730°) is formed by burning calcium in bromine vapour, or by dissolving lime or calcium carbonate in hydrobromic acid and evaporating. The silky needles thus obtained are hydrated, but may be converted to the anhydrous salt by heating. Calcium bromide much resembles the chloride in properties, being deliquescent, and very soluble in alcohol. NaBr and $CaBr_2$ solidify to form two series of solid solutions with a eutectic point at 513°, and on further cooling a reaction takes place at 469°, a compound $NaBr,2CaBr_2$ being formed. KBr forms a single compound $KBrCaBr_2$, represented by a maximum on the freezing-point curve at 637°. There are eutectic points at 544° and 563° respectively (Zeitsch. anorg. Chem. 90, 137).

Calcium iodide CaI_2 may also be prepared by combustion of calcium in iodine vapour, or by solution of lime or the carbonate in hydriodic acid, evaporating and fusing the residue in a closed vessel. Heated in contact with air, it fuses below a red heat, and is decomposed with liberation of iodine vapours and formation of lime.

Liebig (Annalen, 121, 222) recommends decomposition of CaI_2 by K_2SO_4 for preparation of iodide of potassium. To prepare the calcium iodide, 1 oz. of amorphous phosphorus is drenched with 30 oz. hot water, and finely pulverised iodine gradually added with constant stirring as long as it dissolves without colour (quantity thus dissolved being 13½ oz.). The colourless liquid is then decanted from the slight deposit, and made slightly alkaline with milk of lime (8 oz. lime being required); the solution is afterwards strained, and residue of phosphate, phosphite, and hydrate of calcium washed. The solution then contains the calcium iodide, which may, if necessary, be obtained by evaporation in the form of hydrate in deliquescent needles.

A double iodide of calcium and silver of the composition $CaI_2{\cdot}2AgI,6H_2O$ has been prepared by Simpson (Proc. Roy. Soc. 27, 120) by saturating a hot concentrated solution of CaI_2 with moist silver iodide. It crystallises on cooling in long white needles, decomposed by water. The basic salts formed by the alkaline earth metal haloids have been studied by the equilibrium relations in the ternary system between the haloids, the corresponding hydroxides and water. The basic salt CaI_2 $3CaO,16H_2O$ is stable at 25° in contact with solutions containing 28·44 p.c. to 66·68 p.c. CaI_2 (Zeitsch. physikal. Chem. 1917, 92, 59).

Calcium iodate $Ca(IO_3)_2$ is obtained by crystallising mixed solutions of potassium iodate and calcium chloride. The hydrated salt forms four-sided prisms which effloresce in the air, and become anhydrous when heated to 200°. From a solution acidulated with nitric acid, it separates in trimetric crystals. The crystals are soluble in 454 parts water at 18°, and in 102 parts of boiling water, but are insoluble in alcohol. The anhydrous salt, gently heated in a porcelain retort, evolves 14·78 p.c. of oxygen, and 54·07 of iodine, leaving 31·14 p.c. of a residue rich in pentabasic periodate of calcium. Heated more strongly, it evolves more oxygen and iodine, and leaves 20·35 p.c. of a mixture of pentabasic periodate and free lime. Calcium iodate detonates violently when heated on charcoal.

Sonstadt proposes (Eng. Pat. 6304, 1884) to use calcium iodate as an antiseptic.

Periodates of calcium. When the sodium salt NaH_4IO_6 is decomposed by calcium nitrate, a crystalline white precipitate of dicalcium periodate CaH_3IO_6 or $2CaO.3H_2O.I_2O_7$ is obtained. When this salt is heated, water, oxygen, and iodine are given off and pentacalcium periodate $Ca_5I_2O_{12}$ remains (Langlois).

Calcium fluoride CaF_2 is found widely distributed in nature and is known as *fluor-spar.* It is the only common mineral in which fluorine forms one of the principal constituents. It occurs both massive and in beautiful crystals, generally cubes or forms in combination with the cube. It is a common vein mineral, occurring usually in association with metallic ores, barytes, calcite, &c. It presents a variety of colours, sometimes shading into one another as in the beautiful 'Blue John' of Derbyshire. All the coloured specimens lose their colour on heating, green specimens being the most difficult to decolourise completely. Thermo-luminescence is very marked in all naturally coloured crystals, a violet light being emitted in most cases, with decrepitation Free fluorine has been shown to exist in a dark violet fluor spar from Quincié, Dept. du Rhône. Crystallised colourless fluor spar can be coloured deep blue by the β- and γ-rays of radium, and then shows on gentle warming a beautiful green thermo-luminescence which fades and changes into the pale violet light characteristic of all fluor spars. Debierne found that certain dark violet fluor spars smell of ozone. When heated they lose their colour and thermo-luminescence and also yield helium in variable but small quantity. On exposure to radium rays the violet colour was restored. It is also a constituent in small quantities of many plant ashes, of bones, and of the enamel of teeth. When calcium fluoride, obtained by precipitating any soluble calcium salt with fluoride of sodium or potassium, is heated with water slightly acidified with hydrochloric acid, the precipitate is found to consist of microscopic octahedrons.

Calcium fluoride is soluble in about 2000 parts of water at 15°, and is slightly more soluble in water containing carbon dioxide. It dissolves in hydrofluoric acid and in strong hydrochloric acid, and is precipitated in the gelatinous form by ammonia. It is fusible at 902°, and is used as a flux in many metallurgical operations, especially in the reduction of aluminium. It is decomposed at a high temperature by water vapour into lime and hydrofluoric acid. Fusion with alkaline carbonates or hydroxides yields carbonate or oxide of calcium and alkaline fluorides. Strong sulphuric acid, on gently warming, decomposes it, forming calcium sulphate and liberating hydrofluoric acid. At a red heat it is also decomposed by chlorine. After being heated fluor spar phosphoresces in the dark. There is a considerable industry carried on in fluor-spar districts in the carving of ornamental vases and other articles, the brilliantly coloured varieties being especially in demand.

Calcium carbide CaC_2. Wöhler (Ann. Chim. Phys. 125, 120) showed that by the action of carbon on a molten alloy of zinc and calcium, a black mass is obtained, which on contact with cold water liberates various gases. Winkler indicated the reduction of the alkaline earths by magnesium (Ber. 22, 120). Maquenne, in 1892, prepared calcium carbide as an impure amorphous black powder, and Travers obtained it by heating together calcium chloride, sodium, and carbon. It was not, however, until the advent of the electric furnace that it became possible to manufacture a pure carbide suitable for the preparation of acetylene. Moissan (Compt. rend. 138, 243) used a mixture of lime 120 grams, sugar carbon 70 grams, which was heated in the crucible of an electric furnace for 25 minutes with a current of 350 amperes and 70 volts. At the temperature of liquefaction of the lime, this reaction occurs: $CaO+3C=CaC_2+CO$. Pure calcium carbide is crystalline, colourless, and transparent, but the commercial variety, discoloured by iron, is usually brownish-red.

Its characteristic reaction is the decomposition of water in the cold, with the liberation of acetylene and the formation of calcium hydroxide (*v.* Acetylene).

One of the most interesting developments of the manufacture is the production of 'nitrolin,' calcium cyanamide $Ca(CN)_2$, from calcium carbide for manurial purposes. The nitrogen required is obtained from the air by the Linde Company's plant, which produces both nitrogen and oxygen. The union of powdered calcium and nitrogen takes place with the evolution of heat, hence the temperature has to be maintained between 800°-1000°, as at higher temperatures the calcium cyanamide decomposes. The absorption occupies 30 to 40 hours, and the product is a cokelike material which is ground to powder before being placed on the market (*v.* NITROGEN, UTILISATION OF ATMOSPHERIC).

Calcium Carbide, Manufacture of. The commercial manufacture of calcium carbide is credited to Willson in America and Héroult in Europe. It was started in the early eighties of last century, and by progressive development acquired the distinction of being the largest consumer of energy in the electric furnace industry. This continued extension resulted in a better design and increased size of furnace, together with the necessary equipment for handling large quantities of raw materials and for preparing the carbide for the market.

The chief factors which have to be considered in the choice of a site for a carbide factory are supplies of raw material consisting of limestone and coke, or anthracite, and an abundant source of cheap electric power. Large works have consequently been established in places where a practically unlimited supply of water power is available. Hence, most progress in the industry has been witnessed in Norway, where—excepting coal—other demands are amply satisfied.

The raw materials used in the manufacture of calcium carbide should be as pure as possible. Special attention should be paid to obtaining them free from phosphorus, sulphur, and magnesia; silica, iron, and alumina should be present only in small quantities (*v.* Witherspoon, J. Soc. Chem. Ind. 1913, 113).

Phosphorus occurs in limestone as calcium phosphate, and is reduced at the temperature of the furnace, and in the presence of carbon, to calcium phosphide, which, when brought into contact with water, evolves phosphoretted hydrogen. This gas mixes with the acetylene, and when the burners are lighted, causes a haze of phosphorus pentoxide, which is very objectionable. So carefully, however, are the raw materials selected that all commercial carbides are practically free from phosphorus, the average content in acetylene being less than 0·002 p.c. by volume. (For a method of examining commercial carbide for calcium phosphide based on that of Lunge and Cedercreutz, *see* Dennis and O'Brien, J. Ind. Eng. Chem. 1912, 4, 834.)

Sulphur, unless present with considerable amounts of alumina, has little influence on the resulting carbide. Calcium sulphide, formed in the furnace by the reduction of calcium sulphate, does not decompose in the production of acetylene, but in the presence of alumina, aluminium sulphide may be formed, which yields hydrogen sulphide when brought in contact with water. Very little trouble, however, is experienced with sulphur, as the lime and coal used in the manufacture rarely contain a prohibitive quantity.

Magnesia has the peculiar property of interfering with the formation of calcium carbide in the furnace. If more than one p.c. of magnesia be present in the lime and coal, the electrical energy required becomes noticeably so much greater, that raw materials containing such impurity are considered unfit for use. A flux of fluor spar has been used to counteract this effect, but with little success. Magnesia mixed with carbon and heated in the electric furnace does not form a carbide and is highly infusible; under similar conditions barium and strontium oxides form carbides with ease.

Silica, iron oxides, and alumina form silicates, aluminates, and ferro-silicon, which reduce the purity of the carbide and the output of the furnace.

The preparation of the raw materials in carbide manufacture is of much importance, owing to the high temperatures employed in the reduction of the lime. Water in the free state in the coal, or combined as hydroxide in the lime, should be entirely eliminated, its presence reducing the output of the furnace in very serious proportions. The coal is, therefore, thoroughly dried at a low heat in some convenient type of oven or rotary dryer. The limestone, consisting of calcium carbonate, requires a high temperature to drive off the carbon dioxide, and the operation is usually conducted in some type of lime kiln fired by coal or gas.—the Alby works at Odda used producer gas-fired kilns—or the limestone may be burnt in specially constructed chambers, using gases evolved from the manufacture of the carbide. The ingredients were formerly ground fine to ensure a uniform product, but this is now found unneccessary, and the limestone is reduced by crushers to 1–2 inch size, and the coal to ¼–½ inch mesh. They are then weighed and mixed roughly in about theoretical proportions required by the equation $CaO+3C=CaC_2+CO$, or approximately 100 parts by weight of lime to 65 parts by weight of the carbon contents of the coal.

The types of electric furnace which have been used in the manufacture of carbide may be roughly divided into the intermittent and continuous forms. In the first and earlier type the carbide was allowed to solidify in the crucible, and was hence known as the ingot furnace. This, or the pot furnace, of which Borcher's is the simplest type, consists of a large iron crucible lined on the bottom with a layer of carbon, this forming one terminal of the electrical circuit. The other terminal is formed of a carbon rod which is suspended vertically in the crucible, and provided with some form of mechanical hoist to give a vertical motion to the rod and holder, which together may weigh as much as one ton. To start the furnace, the moving electrode is lowered, until on passing a current an arc is formed with the carbon bottom. The mixture of lime and coal previously prepared and stored in a bin above the furnace is fed in around the arc until entirely covered. A current of 2000 ampères and 75 volts was used in the early Willson furnace. The arc being started, interaction soon commences between the lime and the carbon, producing a pool of carbide, which gradually deepens, necessitating frequent lifting of the electrode to keep the current constant. The process is continued until the furnace is full, when the crucible is wheeled out and an empty one substituted. When sufficiently cool, the contents are dumped on to a grating to separate the unconverted mixture, and the ingot removed to a clearing room, where the crust is removed and the block of carbide broken up.

In practice four tons of raw material were handled to produce one ton of carbide, and the process was also unsatisfactory on account of the varying quality of the product, which, though pure carbide in the centre, was only a fritted mixture of lime and coke on the crust. In order to improve both the quality and output the American makers adopted a rotating furnace, of which the Horry furnace is the best-known type. This is built in the form of a spool with wide flanges fastened to the drum, producing three sides of a square in cross-section The fourth side is formed by a removable plate, clamped across the flanges. Two electrodes, suspended vertically, form an arc in the furnace, a single-phase current of 4000 ampères and 75–80 volts being employed. The electrodes are fixed, but the furnace is made to rotate at a peripheral speed of about 6 inches an hour. In operating the furnace a layer of broken coke is placed under the electrodes, the arc is sprung, and the charge of lime and coal fed in until the electrodes are covered. As the carbide is formed the rotation brings the electrodes into contact with a fresh charge, while the fluid carbide slowly solidifies to an ingot shape, and is detached in large blocks at the rear end of the furnace. In a modification the fused carbide is made to pass through a die which separates the fused carbide from the unreduced mixture, and cools the carbide sufficiently to determine its shape, whence it is withdrawn progressively and detached in the form of a pig devoid of crust.

In Europe the early pot furnace was soon changed to a tapping furnace, in which the carbide was heated until sufficiently fluid to be run into cast-iron moulds. The earlier furnaces were similar in form to the pot furnace, with one suspended electrode, but it was difficult to get the desired temperature and fluidity. Two or more electrodes were then introduced, and the progress in electric furnace design for high temperatures followed largely its development in the carbide industry. The furnace, as constructed by Alby in Sweden, used a single-phase alternating current of 1500 kilowatts, and produced 50–60 tons of carbide per week.

The electrodes, which in the early days of the industry were obtainable only in comparatively small sizes, could later be purchased up to 22 inches square and more, and were also used by some manufacturers as an assembly of smaller ones. The working temperature in the furnace attained 3000° C., though the casting temperature may be somewhat lower. To withstand such a great heat the furnace, which is constructed of steel framework and plates, has to be lined with some refractory material, preferably as inert as possible towards the elements of the charge, and, where the heat is most intense, water cooling tubes may be built into the lining. It is necessary also to insulate the electrodes to prevent short circuiting through the furnace construction, as also to make a gas tight joint where the closed form of furnace is employed.

Considerable progress has been made in attaining size and efficiency by the use of multiphase current, which has resulted in advantage not only to the carbide industry but also in the manufacture of ferro silicon and other ferro alloys. According to Helfenstein and Taussig (Seventh Congress of Applied Chemistry), the largest power consumption possible with a built-up electrode amounts to 2500–3000 kw., the current being 30,000–40,000 ampères at 75–95 volts at the electrode. In a three-phase furnace—the only type used for large units—this means a total power consumption of from 7500 to 9000 kw., or 10,000 to 12,000 h.p. In the manufacture of carbide a further step has been taken in the construction of double three-phase furnaces, in which in the same hearth six instead of three electrodes are employed, connected to two separate three-phase units; the power required being from 15,000 to 18,000 kw., corresponding to a production of from 80 to 110 tons of carbide in 24 hours. In this modification there is no increase in loading, but it is interesting as showing that the power capacity so attainable is unlimited, whereas any attempt to increase the power of consumption beyond 2500 to 3000 kw. per electrode is found to be impracticable unless the furnace is operated by entirely special methods.

In open furnaces the heat due to the burning of the gaseous products of the reaction is so great, that even with less than 3000 kw. per electrode special protection against the heat has to be provided both for the workers and the electrical plant. Simultaneously the gases evolved become a serious nuisance in open carbide furnaces, and smoke is developed disproportionately as the power is increased, for which reason it is not advisable to exceed 3000 kw. per electrode. Another obstacle to the use of higher concentration of power is the difficulty of satisfactorily charging the raw materials into the furnace so as to keep the electrodes uniformly covered, any undue exposure leading to fuming, or distillation of material due to overheating.

As the capacity of the furnace is increased the utilisation of the gases produced by the reaction becomes of greater economic moment. In the carbide furnace 70–85 p.c. of the gases is carbon monoxide, with carbon dioxide and water, which are easily removable in practice as the sole impurities. Furnaces are now designed entirely closed in, so that evolved gas can be utilised for heating purposes, and by so doing smoke nuisance and excessive radiation of heat is avoided.

The type of furnace as covered by Helfenstein's patents illustrate the main features of interest in connection with mechanical charging and other general problems of management of the electrical furnace for the manufacture of carbide. Fig. 8 shows an elevation and section of an 8000–10,000 kw. single three-phase furnace. About 8–10 metres above the bottom plate is a charging floor, where the raw material is brought, as in blast furnace plants, by tipping waggons to the charging apparatus at regular intervals. The charging arrangements consist of a large mixing chamber, which can be closed gas tight, communicating with the body of the furnace, through which the central hanging electrode, of 3000–4000 k.g. weight, passes, being thus surrounded on all sides by the mixture. The mixing reservoir, which has a capacity of from 5000 to 7000 k.g., is fed continuously as the material is used in the process through large pipes from the charging floor above. Wide slits provided with gas-tight covers are made in the top of the furnace proper, near the mouth of the reservoir, for observation and control of the process.

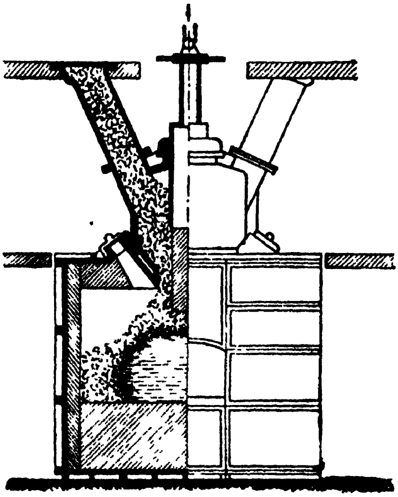


Fig 8.

When no more profitable use of the waste gases is required, their immediate application in preheating the charge can be carried out as illustrated in Fig. 9. The general form of the furnace is the same as Fig. 8. It is seen that in the upper part of the hearth there is a gas-filled corner space bounded by the naturally sloped surface of the raw materials; by blowing or sucking air in at the nozzles, as indicated in the diagram, this space is converted into a combustion chamber, the gases burning in contact with the mixture of material in the hearth. In another Austrian modification the furnace is provided with charging vessels in the form of shafts similar in design to Helfenstein's, but with a branch for taking off the waste gases.

The A.G. works near Cologne, which are capable of producing 200 tons of carbide a day, are described by Allmand and Williams (J. Soc. Chem. Ind. p. 304 R., 1919). The power is obtained from five three-phase turbo generators of 11,250 kw. each, and three smaller ones capable of supplying power and current for seven furnaces. When visited, two of the large generators were working four furnaces, 3000 kw. being consumed on power and light. The furnaces consist of steel plate shells 30 by 14 by 10 feet deep, lined with 18 inches of firebrick, the hearth or crucible being afterwards rammed with carbon concrete. The electrodes 50 by 20 inches cross section, and 7 feet 6 inches to 8 feet in length, were built up of sections 20 by 20 and 20 by 10 inches. Flange, boss, and contact head of each electrode were separately water cooled, and the current was carried by groups of flexible copper wires suspended by chains, each with separate electric motor control. The furnaces were of the open type, the smoke and dust being exhausted from openings in the back wall of the furnace. 260 tons of lime to 185 tons of coke per day were required at full working pressure. The lime was passed through a 4-inch ring, and the coke was in pieces 1 to 3 inches across. The electrode consumption was five kilo. per ton of carbide. One tap hole was tapped in each furnace every 45 minutes by an arc tapper, and each furnace was provided by three tap holes placed below the three electrodes.

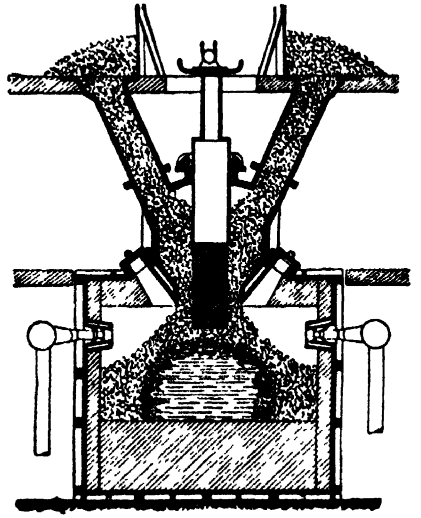


FIG. 9.

The subsequent treatment of the carbide requires special machinery, according to whether the material is to be used for the preparation of acetylene or for the manufacture of cyanamide. In the former case the clean ingots are broken into large blocks and fed into jaw crushers, from whence it is passed for granulation through slow-moving rolls, the object being to attain the desired state of division with a minimum production of dust. The crushed material is sized on trommels or rotary screens, which deliver the product in sizes varying from large lumps 8 by 4 inches, for the manufacture of acetylene on a large scale, to 16–30 mesh size, for automobile lamps, &c. A sheet-iron plant, where steel drums and air-tight cans are manufactured for storing and transport of the carbide, is a necessary part of every works. The standard packages are 100, 110, 200, 220 lbs. net weight of carbide, and small tins from 1 to 25 lbs. for lamps.

The largest use of calcium carbide is for making acetylene, but the cyanamide (*q.v.*) industry is dependent on calcium carbide for its manufacture. For this purpose it is necessary to reduce the material to a fine state of division, and to prevent oxidation and explosion it is usually performed in an atmosphere of nitrogen.

The manufacture of calcium carbide at prices prevailing in normal times depends upon the supply of cheap electric power. Norway, having abundance of water power and deposits of suitable limestone, has long been the largest producer of carbide. According to C. Bingham (J. Soc. Chem. Ind. March 15, 1918), to produce a ton of carbide requires 4250 units of electric power, this figure including not only the current required for the furnaces themselves, but that absorbed by transformers and loads, as also that consumed by motors to drive crushers, elevators, pumps, and drum-making plant. The cost in Norway with cheap water power amounted in normal times to 22*s.* to 25*s.* per ton of carbide, and its selling price was £10 15*s.* in England.

The only factory in Great Britain was at Thornhill, Yorks, which, owing to lack of electric power, was removed to Manchester, where a large plant has been built. At 0·4*d.* per unit the cost in Great Britain for current alone would be £6 3*s.* 4*d.* per ton of carbide, but if the process was run in connection with blast furnaces and coke ovens having a surplus of electric power or gas for the manufacture thereof, it is calculated that this figure could be reduced to £2 10*s.* per ton of carbide, reckoning 0·11*d.* per unit for depreciation and running cost, and 2*d.* per 1000 cu. ft. for gas used in gas engines consuming 27 cu. ft. per kw. hour, or for the 1250 units mentioned, a cost of 19*s.* 2*d.*

The Nitrogen Products and Carbide Co., Ltd., amalgamated with the Alby United Carbide Factories, Ltd., have acquired the St. Helens Colliery and Coke Ovens, Workington, with the object of producing carbide and nitrolim in this country on an economical basis. Electrodes are being produced at Hebburn-on-Tyne.

Calcium carbonate $CaCO_3$ occurs naturally in the forms of limestone, chalk, marble, and calcite; it also constitutes the principal ingredient in egg-shells, mollusc-shells, and coral. It is formed when the oxide or hydroxide is exposed to moist air containing carbon dioxide, but is not produced by the action of dry carbon dioxide on dry lime. It may be obtained in the pure state by dissolving chalk, or marble, or calcined oyster-shells in hydrochloric acid, precipitating the alumina, oxide of iron, and earthy phosphates by ammonia or milk of lime, filtering, then precipitating the calcium by ammonium carbonate, washing and drying.

Calcium carbonate is dimorphous, crystallising in the hexagonal system as calcite (*q.v.*) and in the rhombic system as aragonite (*q.v.*).

A litre of water dissolves about 18 milligrams of calcium carbonate. The solution has a slight alkaline reaction. Gothe (Chem. Zeit. 39, 305) gives the solubility of $CaCO_3$ in water free from CO_2 as being 31·0 mg. per litre. It is increased by the presence of chlorides, nitrates, and sulphates in the water, but decreased by alkaline carbonates, and by chlorides, nitrates, and sulphates of the alkaline earths. When boiled with water $CaCO_3$ (Gazz. chim. ital. 47, ii. 49) slowly dissociates with evolution of CO_2. This dissociation stops at a certain point, and is prevented, if a solution of $Ca(OH)_2$ (saturated at the ordinary temperature) is added to the boiling calcium carbonate in water in the proportion of 15 c.c. per litre. Sodium carbonate (0·05 gram per litre) prevents dissociation. Seyler and Lloyd (Chem. Soc. Trans. 111, 994) find that the ionic solubility product of calcium is $[Ca^{\cdot\cdot}]\cdot[CO_3{}^{\cdot\cdot}]=71{\cdot}9\times10^{-10}$, which gives $[Ca^{\cdot\cdot}]=14{\cdot}6\times10^{-6}$ for a saturated solution $CaCO_3$ in pure water. In this solution the carbonate is hydrolysed to the extent of 66 p.c. Water containing carbonic acid dissolves it much more readily, forming the acid carbonate $CaH_2(CO_3)_2$, which is known only in solution. Solubility at higher pressures in water containing carbonic acid follows the law of Schloesing pretty closely (Engel, Compt. rend. 101, 949). The solubility increases under an increase of pressure only up to 3 grams per litre according to Caro. One litre of water saturated with carbon dioxide dissolves 0·7 gram of the carbonate at 0°, but 0·88 gram at 10°. The solubility of calcite in water, determined at different temperatures by bubbling air containing 3·18 parts of CO_2 per 10,000 until saturation occurs, expressed in parts of $CaCO_3$ per million is: at 10°, 82; 21°, 60; 22°, 57; 23°, 57; 30°, 55. Cavazzi (Gazzi chim. ital. 46, ii. 122) finds that the maximum quantity of $CaCO_3$, which after prolonged shaking, dissolves at 0° in one litre of water saturated with CO_2 and maintained so in the presence of the gas at atmospheric pressure is 1·56 grams (2·5272 grams $Ca(HCO_3)_2$); at 15°, 1·1752 $CaCO_3$ (1·9038 $Ca(HCO_3)_2$). A supersaturated solution is obtainable, containing 2·29 grams $CaCO_3$ per litre. This acid carbonate plays a most important part in nature, for whenever water containing carbonic acid comes in contact with carbonate or silicates of calcium, the calcium is gradually converted into this soluble form, and is therefore found in almost all natural waters. Hence also the deposits in kettles and boilers; the formation of which may be prevented by the addition of ammonium chloride to the water.

Calcium carbonate, when heated to full redness in open vessels, is decomposed into lime and carbon dioxide. The decomposition commences at a low red heat, and in a current of air, or better steam, the temperature of dissociation is lower still. The tension of dissociation becomes equal to the pressure of the atmosphere, according to Le Chatelier (Compt. rend. 102, 1243), at about 812°. If heated rapidly, the stationary temperature of dissociation is 925°. At 547° the tension of dissociation is 27 mm.; at 610°, 46 mm.; at 625°, 56 mm.; at 740°, 245 mm.; at 810°, 678 mm.; and at 865°, 1333 mm. If the carbonate be ignited in a closed vessel, it fuses, resolidifying to a mass of marble-like calcite. According to Becker (Jahrb. Min. 1886, 1, Ref. 403), any form of $CaCO_3$, even at a low pressure, is changed on heating in a closed space with exclusion of air into the rhombohedral form without fusion. The crystalline forms of calcium carbonate dissociate very slowly below 400°; at this temperature the dissociation pressures are of the order of 0·003–0·009 mm. At 425° aragonite is transformed into calcite within an hour when heated in a vacuum. Besides the two well-known forms a third crystalline form, referred to as $\mu CaCO_3$ (Merwin and Williamson, Amer. J. Sci. 41, 473), is obtained by precipitation at 60° along with calcite and aragonite. It has D. 2·54, and can be separated from calcite D. 2·71, and aragonite D. 2·88 by flotation in a liquid D. 2·6. If small quantities of the precipitated carbonate are thrown into a fused mixture of sodium and potassium chlorides in equivalent proportions, no carbon dioxide is evolved, but the carbonate becomes crystalline calcite, usually in aggregations of crystals like snow crystals (Bourgeois, Bull. Soc. chim. [2] 37, 447).

Pentahydrated calcium carbonate
$CaCO_3,5H_2O$.

The evaporation of natural solutions of the acid carbonate generally results in the deposition of the ordinary carbonate, forming the stalactites and stalagmites of caverns, travertine, and other forms of deposit; but sometimes the solution yields six-sided rhombic prisms of the composition $CaCO_3,5H_2O$. These crystals are often found in pumps and pipes leading from wells, also adhering to the confervæ in ponds. They keep unaltered under water at 20°, but at slightly higher temperatures lose their transparency and water of crystallisation In air they crumble to powder through loss of water (Pfeiffer, Arch. Pharm. [2] 15, 212). This salt, according to Pelouze (Ann. Chim. Phys. [2] 48, 301), is obtained in small acute rhombohedra, sp.gr. 1·783, by boiling lime in a concentrated solution of sugar, starch, or gum, and leaving the solution for some months in a cold place. Becquerel, by exposing a solution of lime in sugar water to a voltaic battery of 12 cells, obtained crystals of the same composition, but in form of rhombic prisms.

Basic carbonates of lime. Calcium oxide commences to absorb carbon dioxide at a temperature of 415°, forming a basic carbonate of the composition $2CaO{\cdot}CO_2$ (Birnbaum and Mahu, Ber. 12, 1547).

Raoult (Compt. rend. 92, 1457) shows that when freshly burnt lime is heated in a current of carbon dioxide, it glows strongly, forming $2CaO{\cdot}CO_2$, which does not disintegrate in moist air, and does not take up water from steam at 200°. When finely powdered and treated with a little water, it hardens like hydraulic cement. The hydrated product has the composition $CaCO_3{\cdot}Ca(OH)_2$. On heating to dull redness, it loses water and is converted into a mixture of $CaCO_3$ and CaO.

When burnt lime is heated in contact with carbon dioxide for several days, the basic salt $2CaCO_3{\cdot}CaO$ is obtained, which still absorbs CO_2, forming a third salt $3CaCO_3{\cdot}CaO$. The carbon dioxide continues to be absorbed, however, and appears eventually to form the normal carbonate.

Calcium nitride Ca_3N_2 is best obtained by passing dry nitrogen over metallic calcium contained in a nickel boat and tube heated to bright redness. Two to three hours are required, and the resulting material is fritted and possesses a brownish-red colour. Its fusion point is about 1200°; sp.gr. 2·63 at 17°. When thrown into water it produces a lively effervescence, yielding ammonia and calcium hydroxide

$$Ca_3N_2+6H_2O=3Ca(OH)_2+2NH_3$$

(Moissan, Ann. Chim. Phys. [7] 18, 289). The nitride, heated in a current of hydrogen, gives a compound having the formula $Ca_3N_2H_4$ (Monatsh. 34, 1685).

Calcium ammonium $Ca(NH_3)_4$ is formed when a current of dry ammonia gas is passed over metallic calcium, maintained at a temperature of 15° to 20°. It possesses a brownish-red colour, and takes fire when exposed to air.

Calcium amide $Ca(NH_2)_2$. Calcium ammonium slowly decomposes, forming transparent crystals of calcium amide, hydrogen and ammonia being evolved.

Calcium imide CaNH is formed by passing equal volumes of hydrogen and nitrogen over heated calcium. It has not been obtained pure (Monatsh. 34, 1685).

Calcium nitrite $Ca(NO_2)_2.H_2O$ is prepared by decomposing a boiling solution of silver nitrite with lime-water, treating the filtrate with sulphuretted hydrogen and carbonic acid to remove excess of silver and calcium, and evaporating at a gentle heat. It crystallises in deliquescent prisms insoluble in alcohol.

Calcium nitrate $Ca(NO_3)_2,4H_2O$ occurs as a silky efflorescence in limestone caverns, especially those of Kentucky, also on the walls of places where there is much organic refuse. It is found in many well waters, being derived from the soil. It is extremely deliquescent and soluble, and causes rapid disintegration of mortar, and hence is called 'saltpetre rot.' It may be prepared by dissolving the carbonate in nitric acid, the solution depositing on slow evaporation monoclinic six-sided prisms terminated by acute pyramids of the above composition. On evaporating the solution to dryness, the anhydrous salt of sp.gr. 2·472 is obtained, possessing a warm bitter taste and readily soluble in water and alcohol. On heating more strongly, it becomes phosphorescent, as noticed by Baldwin in 1674, and hence is termed *Baldwin's phosphorus*. At a higher temperature, oxygen and nitric peroxide are evolved, and with combustible bodies detonation occurs. The nitrate is formed with liberation of nitrogen when nitrogen peroxide acts on lime, whatsoever be the conditions of temperature $2CaO+5NO_2 \rightarrow 2Ca(NO_3)_2+0{\cdot}5N_2$ It is extensively prepared on the Continent for the manufacture of nitre by mixing vegetable and animal refuse with chalk, marl, cinders, &c., moistening from time to time with liquid stable manure, and exposing to the air for two or three years, when the mass is lixiviated and the crude nitrate of calcium decomposed by carbonate, sulphate, or chloride of potassium. Large quantities of calcium nitrate are now produced by the Haber process. At the Svälgfos works, Notodden (55,000 h.p.), and the Ryukan works (120,000 h.p., to be increased to 300,000 h.p.), the nitrous fumes from the Birkeland and Eyde furnaces or the Schonherr furnaces are absorbed in granite towers and the waters neutralised by limestone. The wet method of absorption is now being replaced by a dry method, which does not necessitate the use of towers, the nitrous fumes being absorbed by passing over lime kept at a temperature of about 300°. The conversion to ammonium nitrate cannot be accomplished satisfactorily by the interaction of ammonium sulphate and calcium nitrate owing to the fine condition of the calcium sulphate, but this becomes crystalline if heated in an enclosed vessel to 150°–175°, which can then be readily separated.

Calcium phosphide. Moissan (Compt. rend. 128, 787) prepared calcium phosphide from pure crystallised calcium and red phosphorus. The two bodies were placed apart in a tube which was exhausted and the phosphorus was gently heated. The vapours evolved combined with the calcium with incandescence. He also obtained it by reduction of pure calcium phosphate with carbon in an electric furnace, using 310 parts and 96 parts respectively of the ingredients and a current of 950 ampères and 45 volts. So obtained, it is a brownish-red body, crystalline when prepared in the electric furnace. Its characteristic reaction is the decomposition of water in the cold with the production of calcium hydroxide and hydrogen phosphide. Prepared by either of the above methods, it has the composition Ca_3P_2.

Thenard (Ann. Chim. Phys. [3] 14, 12) obtained calcium phosphide mixed with phosphate by passing the vapour of phosphorus over red-hot lime. The substance may be prepared on a larger scale by filling a crucible with a hole in its base with pellets of lime, and placing it upon the grate of a furnace. A flask containing phosphorus is placed below the grating with its neck passing into the hole of the crucible. When the lime has been heated to redness, the phosphorus is gradually heated so that its vapour passes through the lime. The brown mass is stated by Gmelin (Handb. 3, 188) to be a mixture of monocalcium phosphide and tricalcium phosphate.

When thrown into water, the product is instantly decomposed with evolution of spontaneously inflammable phosphoretted hydrogens.

Owing to this property, calcium phosphide is utilised for the production of signal fires at sea. The manufacture is carried on in an arrangement similar to the above, the crucibles being larger and divided by a false perforated bottom into two compartments, in the upper of which the pieces of lime are raised to a red heat, the phosphorus placed in the lower compartment being afterwards volatilised by the heat radiated from above. In about 6 hours, a charge, yielding 20 lbs. of product, is finished. The brown stony mass is immediately worked up into the 'lights.' These consist of cylindrical tinned-iron boxes, the lower half of which is filled with about 16 oz. of the fragments of phosphide.

Two small circular portions of the upper and under surfaces of metal are formed of soft lead, so that they may be pierced by a knife just before being thrown overboard. The tins are supported by a wooden float when in use. The water enters below and the gas issues from the upper outlet, burning with a flame 9 to 18 inches high, lasting about half an hour. Larger but similar 'lights' are prepared to be placed in a bucket of water on deck. In the British Navy torpedo practice, a peculiar form of the phosphide is also used.

Calcium phosphite $CaHPO_3,H_2O$ separates as a crystalline crust from a solution of the ammonium salt mixed with calcium chloride. It is sparingly soluble in cold water, and the solution decomposes when heated, depositing a basic salt, an acid salt remaining dissolved. It gives off its water at 100°. It is a white crystalline powder, which, on heating, evolves spontaneously inflammable phosphoretted hydrogen, accompanied by slight detonations. At a certain temperature, it becomes incandescent, and leaves a residue of calcium phosphate.

An acid phosphite $CaH_4(PO_3)_2,H_2O$ is obtained as a crystalline crust by acting upon marble with aqueous phosphorous acid as long as carbon dioxide escapes. The crust consists of needle-shaped crystals soluble in water, and losing their water at 100°.

Calcium hypophosphite $Ca(PO_2H_2)_2$ or $CaH_4(PO_2)_2$ is used medicinally, and is prepared by boiling phosphorus with milk of lime

$$3Ca(OH)_2+2P_4+6H_2O=2PH_3+3CaH_4(PO_2)_2.$$

On evaporation the hypophosphite is obtained in monoclinic flexible prisms insoluble in alcohol. When heated it evolves phosphoretted hydrogen and water, leaving calcium pyrophosphate.

Calcium orthophosphate $Ca_3(PO_4)_2$ occurs pure in the mineral *osteolite*, and as

$$Ca_3(PO_4)_2,2H_2O$$

in *ornithite*. Combined with calcium fluoride or chloride, it occurs in nature as *apatite*

$$3Ca_3(PO_4)_2+CaF_2$$

in which form it is found in large crystals in the metamorphic limestones at Burgess, Ontario, Canada. The massive variety, *phosphorite*, is mined on a large scale at Odegarden, Norway. In certain apatites, the CaF_2 is more or less replaced by $CaCl_2$. Specimens of apatite and phosphorite are occasionally coloured brown, mauve, and green, and become colourless on heating. Apatite is phosphorescent when heated, especially after exposure to radium.

Calcium phosphate also forms a principal constituent of the coprolites frequently found in extensive beds in the stratified rocks. This material forms the principal source of the rock phosphate of commerce. It is the chief inorganic material of bones, forming about 80 p.c. of burnt bones.

It is obtained in the amorphous state by precipitating an ammoniacal solution of calcium chloride with excess of hydrogen disodium phosphate. The precipitate is gelatinous, but dries up to a white earthy powder, nearly insoluble in water, but is decomposed by long boiling into an insoluble basic salt of the composition

$$Ca_3(PO_4)_2 \cdot Ca_2(PO_4)OH$$

and a soluble acid salt. This reaction also occurs slowly in the cold. Calcium phosphate is also soluble in water containing carbonic acid (1 part in 1789 parts of water saturated with carbon dioxide), ammonium salts, sodium nitrate, sodium chloride, and other salts. Its absorption by the roots of plants is therefore promoted by the agency of saline solutions.

Bassett has shown that only two phosphates more basic than dicalcium phosphate exist; these are tricalcium phosphate $Ca_3P_2O_8$ and hydroxy apatite $(Ca_3P_2O_8)_3,Ca(OH)_2$. The latter is the only stable solid phase over a range of acidity of great practical importance, as it can exist in faintly acid, neutral, or alkaline solutions. It is probable that this compound is the only calcium phosphate that can permanently exist under normal soil conditions. Bone phosphate is considered to be a mixture of hydroxyapatite and calcium carbonate, with small amounts of absorbed bicarbonates of sodium, potassium, and magnesium.

The melting-point of calcium phosphate is 1550°. It is not reduced by CO, but H reduces it at 1300° to a mixture of CaO and phosphorus. Carbon begins to reduce it at 1400°. It is not decomposed by silica in a neutral atmosphere, but a chemical combination occurs at 1150°, and the product is completely reducible by carbon. The compound has the composition $3CaO,3SiO_2,P_2O_5$, and is indicated by a strong maximum on the freezing-point curve of the system calcium-phosphate calcium-silicate. Two compounds $2,SiO_2,P_2O_5$, $3SiO_2,P_2O_5$, have also been isolated, the latter melting in the oxyhydrogen flame.

Freshly precipitated calcium phosphate combines with sulphur dioxide, becoming soluble in water. On heating the solution, some of the gas is liberated and a crystalline precipitate, having the composition $Ca_3SO_2P_2O_8,2H_2O$, is formed, a compound which is very stable (Ber. 15, 1441).

Calcium orthophosphate may be obtained in the crystalline form by heating dicalcium pyrophosphate with water, whereby it is resolved into phosphoric acid and tricalcium phosphate, which separates in rectangular plates

$$3Ca_2P_2O_7+3H_2O=2Ca_3(PO_4)_2+2H_3PO_4.$$

Tricalcium phosphate is not decomposed by ignition.

Dicalcium orthophosphate $Ca_2H_2(PO_4)_2$. An aqueous solution of phosphoric acid acts on precipitated chalk, forming small needle-shaped crystals of dicalcium phosphate. Dried at 100°, the salt contains $5H_2O$, which it does not lose below 115°. It is soluble in ammonium citrate, Boiled with water, it is partially decomposed into tricalcium phosphate.

On mixing boiling solutions of sodium phosphate, calcium chloride, and acetic acid,

$$Ca_2H_2(PO_4)_2,H_2O$$

is formed; if the solutions are mixed in the cold, $Ca_2H_2(PO_4)_2,5H_2O$ is formed (Millot, Bull. Soc. chim. [2] 33, 194). The salt is also formed (Joly and Sorrel, Compt. rend. 118, 741) when saturated solutions are mixed in the cold if hydrochloric acid is added.

When a solution of calcium chloride is mixed with one of ordinary sodium phosphate, a white crystalline precipitate of $Ca_2H_2(PO_4)_2,4H_2O$ is thrown down. It is this salt which is occasionally deposited from wine in stellar aggregates. According to Becquerel and Berzelius, a trihydrate may also be obtained. These different results as regards water of crystallisation are probably owing to the fact that the precipitates vary in amount of water and solubility in acids according to the conditions of their precipitation.

Monocalcium phosphate $CaH_4(PO_4)_2$ is obtained in rhombic tables by dissolving either of the former phosphates in phosphoric acid and allowing the solution to spontaneously evaporate. It has a strong acid reaction, and deliquesces in air, dissolving readily in water. A small quantity of water decomposes it, forming insoluble dicalcium phosphate and free phosphoric acid. If cold, the hydrate $Ca_2H_2(PO_4)_2,4H_2O$ is formed; if hot, the same salt, free from water. is precipitated.

Monocalcium phosphate fuses on heating, giving up its water, and when heated to 200° it parts with the elements of water, leaving a mixture of calcium pyrophosphate and metaphosphoric acid

$$2CaH_4(PO_4)_2 = Ca_2P_2O_7 + 2HPO_3 + 3H_2O.$$

When the mixture is heated to a still higher temperature, pure calcium metaphosphate remains.

Superphosphate of lime is a mixture of monocalcium phosphate and calcium sulphate, which is manufactured as a manure. It is prepared by acting on bone-ash, rock phosphate, phosphorites, or other mineral phosphates with two-thirds their weight of sulphuric acid:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4.$$

Besides its use as a manure for root-crops, it is used in the manufacture of phosphorus (*v.* FERTILISERS).

Calcium pyrophosphate $Ca_2P_2O_7$ is prepared by action of aqueous pyrophosphoric acid upon lime water, or sodium pyrophosphate upon calcium chloride. If the precipitate thus obtained is dissolved in sulphurous acid and the solution heated, the salt separates as a crystalline crust. The crystals contain four molecules of water.

Calcium metaphosphates. The monosalt $Ca(PO_3)_2$ is obtained by dissolving calcium carbonate in orthophosphoric acid, evaporating, and heating the residue to 316°. It is an insoluble white powder.

The dimetaphosphate $Ca_2(PO_3)_4,4H_2O$ is obtained pure in the crystalline form by precipitating the corresponding alkali salt with excess of calcium chloride. It is insoluble in water, but is decomposed by strong sulphuric acid. A double dimetaphosphate of calcium and ammonium $Ca(NH_4)_2(PO_3)_4,2H_2O$ is obtained in spicular crystals by mixing a solution of calcium chloride with excess of the ammonium salt. It is insoluble in water.

Phosphato-chlorides of calcium are obtained by evaporating solutions of tricalcium phosphate in hydrochloric acid. A saturated solution, on spontaneous evaporation, deposits rhomboidal plates of $7CaH_4(PO_4)_2{\cdot}CaCl_2,14H_2O$. If the solution is evaporated over the water-bath, dicalcium phosphate is first deposited, then, on further evaporation, the above phosphatic chloride comes down, and afterwards white scales of $CaH_4(PO_4)_2{\cdot}CaCl_2,H_2O$. When a solution of dicalcium orthophosphate in hydrochloric acid is saturated at ordinary temperatures with tricalcium phosphate, then mixed with half the quantity of hydrochloric acid already contained in it, and evaporated, on cooling below 6° crystals separate out of the composition

$$4CaH_4(PO_4)_2{\cdot}CaCl_2,8H_2O$$

(Erlenmeyer, J. 1857, 146).

Calcium silico-phosphate. According to Carnot and Richard (Compt. rend. 97, 316), the brownish-black slag, formed in working the Thomas-Gilchrist process at Joeuf (Meurthe-et-Moselle), is covered with black crystals, some slender needles, others right rhombic prisms with brilliant faces, frequently aggregated in columnar masses terminating in vitreous, translucent, blue crystals. Similar blue crystals are found in the cavities, possessing the constant composition $8P_2O_5{\cdot}8SiO_2{\cdot}Al_2O_3{\cdot}FeO{\cdot}36CaO$, essentially a calcium silico-phosphate

$$Ca_3(PO_4)_2 + Ca_2SiO_4.$$

Calcium arsenates. Dicalcium arsenate occurs native as *haidingerite* $Ca_2H_2(AsO_4)_2,H_2O$, and *pharmacolite* $Ca_2H_2(AsO_4)_2,5H_2O$, and may be prepared by adding a solution of disodium arsenate to excess of calcium chloride. The tetrahydric arsenate obtained by addition of lime water to arsenic acid is soluble, while the tricalcium arsenate is insoluble in water, and may be prepared by precipitating calcium chloride with trisodium arsenate. On evaporating a hydrochloric acid solution of calcium ammonium arsenate with platinum chloride, the mass left on ignition of the platinochloride is found to contain fine white prisms of the tricalcium orthoarsenate $Ca_3(AsO_4)_2$ insoluble in acids. The metaarsenate $Ca(AsO_3)_2$ is formed as an insoluble crystalline powder when mixtures of arsenious anhydride and calcium carbonate are ignited.

According to R. H. Robinson (J. Agric. Res. 1918, 13, 281), pure calcium hydrogen arsenate ($CaHAsO_4,H_2O$) may be prepared by pouring an acidified solution of calcium chloride into an acidified solution of sodium hydrogen arsenate. It forms a heavy voluminous precipitate which may be obtained crystalline. It becomes anhydrous at 175°. Tricalcium arsenate $Ca_3(AsO_4)_2,2H_2O$ may be prepared by pouring an alkaline calcium chloride solution into an alkaline sodium hydrogen arsenate solution, when a heavy voluminous sparingly soluble precipitate of sp.gr. 3·23 is formed.

Calcium ammonium arsenate

$$CaNH_4AsO_4,7H_2O$$

is produced by mixing a hot solution of arsenic acid in excess of ammonia with calcium nitrate or chloride, when it crystallises on cooling in tables. In a vacuum over sulphuric acid, they become $Ca_2(NH_4)H_2(AsO_4)_2,3H_2O$, and when dried at 100° have the composition

$$Ca_8(NH_4)H_3(AsO_4)_6,3H_2O$$

On ignition they are converted into calcium pyroarsenate $Ca_2As_2O_7$ (Bloxam, Chem. News, 54, 168).

Another salt, $Ca(NH_4)_2H_2(AsO_4)_2$, is obtained by adding excess of ammonia to a solution of dicalcium arsenate in nitric acid, as a flocculent precipitate, soon becoming a mass of needles. The same salt is obtained in crystals belonging to the regular system when the solution of the dicalcium salt is only partially precipitated and allowed to stand; hence it appears to be dimorphous (Baumann).

Calcium silicide was obtained by Moissan by heating calcium oxide with excess of silicon in a carbon tube by means of the electric furnace. It forms greyish crystals, sp.gr. 2·5, which are slowly decomposed by water with evolution of hydrogen.

Tamaru (Zeitsch. anorg. Chem. 62, 81) found that molten silicon is miscible with molten calcium in all proportions.

Kolb (Zeitsch. anorg. Chem. 64, 342), by heating together calcium and silicon, obtained two silicides according to the component in excess. The products contain 53·5 p.c. and 36·68 p.c. silicon respectively, corresponding approximately with the formulæ Ca_6Si_{10} and $Ca_{11}Si_{10}$. Both silicides are crystalline, evolve hydrogen with acetic acid, and evolve spontaneously inflammable hydrogen with dilute hydrochloric acid. Silicones are obtained with strong hydrochloric acid. Both silicides absorb nitrogen near 1000°, the products having the respective compositions $CaSi_2N_2$ and $Ca_{11}Si_{10}N_{10}$.

Calcium silicates. Calcium oxide is an important base in a large number of natural silicates, and is the principal basic constituent of the following minerals *Wollastonite* $CaSiO_3$ or tabular spar, occurring in monoclinic crystals; *okenite* $CaH_2(SiO_3)_2,H_2O$; *xonalite*

$$4CaSiO_3,H_2O;$$

gurolite $Ca_2H_2(SiO_3)_3,H_2O$; and *apophyllite* $4CaH_2(SiO_3)_2{\cdot}KF,4H_2O$.

Gorgeu (Compt. rend. 99, 256) obtained artificial wollastonite by fusing 1 gram of silica with 15 grams calcium chloride and 3 grams common salt at a cherry-red heat in a current of moist air for half an hour.

Doelter (Jahrb. Min. 1886, 1, 119) found that in absence of steam, a hexagonal $CaSiO_3$ is always formed; hence wollastonite must have been formed in presence of steam. Calcium silicate is therefore dimorphous.

Rankin and Wright (Amer. J. Sci. 39, 1) have examined the system $CaO-Al_2O_3-SiO_2$. The melting-points of the three components are 2570° for lime, 2050° for alumina, and 1625° for cristabolite, the high temperature modification of silica. Of the binary systems involved alumina and silica form one compound, sillimanite Al_2SiO_5, whilst lime and alumina form four distinct compounds, $Ca_3Al_2O_6$, $Ca_5Al_6O_{14}$, $CaAl_2O_4$, and $Ca_3Al_{10}O_{18}$. The third binary system, lime-silica, also gives rise to four compounds, Ca_3SiO_5, Ca_2SiO_4, $Ca_3Si_2O_7$, and $CaSiO_3$, the first mentioned of which, however, does not separate from the fusion. In the ternary system three compounds exist, but only anorthite $Ca_2Al_2Si_2O_8$ and $Ca_2Al_2SiO_8$ (? pure gehlenite) are stable at their melting-point, the third $Ca_3Al_2SiO_8$ being unstable. The above compounds do not form solid solutions to any extent, and the authors did not detect in the crystallisations the eutectic (β) structure commonly seen in alloys.

On precipitating the solution of any calcium salt with sodium or potassium silicate, the silicates $2CaO{\cdot}9SiO_2,3H_2O$ and $CaO{\cdot}SiO_2$ have been obtained by Lefèvre and Von Ammon respectively.

Gorgeu (Compt. rend. 99, 256) obtained two chlorosilicates by heating to a high temperature silica and calcium chloride in proportion of one molecule to seven in presence of water vapour. The first, $2CaO{\cdot}SiO_2{\cdot}CaCl_2$, forms birefractive rhombic plates. The second, $CaO{\cdot}SiO_2{\cdot}CaCl_2$, forms hexagonal plates, and is produced more rapidly than the former, which requires prolonged heating. Both compounds are decomposed by water.

Calcium boride CaB_6 was obtained by Moissan and Williams by heating quicklime with boron in an electric furnace, and by reducing calcium borate with aluminium in the presence of carbon, then washing with hydrochloric and hydrofluoric acids and ether. It is a black crystalline body; sp.gr. 2·33. Nitric acid attacks it vigorously.

It is also formed (Ber. 46, 1885) when calcium metaborate (30 grams) is reduced by means of calcium (50 grams), the theoretical quantity of calcium boride being produced. The reaction product is extracted with dilute acetic acid, and then dilute HCl and hot water. So obtained it is a light brown micro-crystalline powder $D^{18}=2{\cdot}11$.

Calcium borate occurs in nature in several combinations. The best known is colemanite $HCa(BO_2)_3,2H_2O$, which crystallises in beautiful monoclinic prisms.

Calcium silicoborate $CaO{\cdot}2SiO_2{\cdot}CaB_2O_4$ occurs with one molecule of water as *datholite*, and with two molecules of water as *botryolite*.

Calcium titanate or $CaTiO_3$ occurs in nature as *perovskite*.

Calcium silicotitanate $CaSiTiO_5$ is a common constituent of many igneous and metamorphic rocks, and is known as *titanite* or *sphene*. Synthetic titanite forms blue crystals (melting-point 1221°), which usually enclose small crystals of perovskite (Zeitsch. anorg. Chem. 73, 293).

Calcium monosulphide CaS. Perfectly dry lime remains unaltered on passing over it a current of dry sulphuretted hydrogen; but on hydrating the lime and again passing the gas, calcium sulphide is formed:

$$Ca(OH)_2+H_2S=CaS+2H_2O.$$

The most favourable temperature is 60° (Veley, Chem. Soc. Trans. 1885, 478).

It may also be prepared by heating the sulphate with coal or charcoal, or by action of carbonic oxide at a red heat:

$$CaSO_4+4CO=CaS+4CO_2.$$

It may be prepared in the crystalline state by direct reduction of the sulphate with carbon in the electric furnace; Müller (Cent. Min. 1900, 178) has obtained it in small cubes.

Anhydrous calcium sulphide is a white powder which emits a smell of SH_2 in the air. It turns yellow on moistening, due to the formation of oxidised products. It is but sparingly soluble in water, and is decomposed by boiling water, with formation of hydroxide and sulphydrate of calcium $2CaS+2H_2O=Ca(HS)_2+Ca(HO)_2$. Suspended in water, it is readily decomposed by carbonic acid, with formation of calcium carbonate and sulphuretted hydrogen

$$CaS+H_2O+CO_2=CaCO_3+H_2S.$$

After being heated, calcium sulphide shines in the dark, and was long known as *Canton's phosphorus*.

According to Verneuil (Compt. rend. 103, 600), calcium sulphide with a violet phosphorescence may be prepared as follows: 20 grams of finely powdered lime, obtained by heating the shells of *Hypopus vulgaris*, is intimately mixed with 6 grams of sulphur and 2 grams of starch, and 8 c.c. of a solution containing 0·5 gram basic bismuth nitrate and 100 c.c. of absolute alcohol acidified with a few drops of hydrochloric acid are added. The mixture is exposed to the air until most of the alcohol has evaporated, and is then heated to cherry redness for 20 minutes. When completely cooled, the upper layer of calcium sulphate is removed, and the calcined mass powdered and again heated for 15 minutes. The violet phosphorescence of the product is due to the trace of bismuth. 0·1 p.c. of sulphides of antimony, cadmium, mercury, tin, copper, lead, uranium, platinum, or zinc imparts a bluish- or yellowish-green tint to the phosphorescence. Manganese produces an orange shade. A mixture of 100 parts lime, 30 parts sulphur, 10 of starch, and 0·035 of lead acetate yields a sulphide with a beautiful yellowish-green phosphorescence.

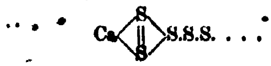
Pure calcium carbonate mixed with 2 p.c. sodium carbonate, and 0·02 p.c. common salt, heated with 30 p.c. sulphur and 0·02 p.c. bismuth nitrate, yields a similar product to that obtained by use of *Hypopus* shells. Pure calcium sulphide does not phosphoresce; the phenomenon is due to small quantities of impurities; thus in the last mixture it has been shown by Verneuil to be due to simultaneous presence of traces of bismuth oxide, sodium carbonate and chloride, and calcium sulphate.

These phosphorescing varieties of calcium sulphide are utilised in the manufacture of luminous paints. Abney (Phil. Mag. [5] 13, 212) found that the emission spectrum showed greatest luminosity between G and F, and a feebler one extending from between E and F as far as the red. The rays of the electric light somewhat beyond H on one side and G on the other are most active in exciting phosphorescence.

Calcium disulphide CaS_2 is deposited in yellow crystals of the composition $CaS_2,3H_2O$ from the solution obtained by boiling sulphur with milk of lime and filtering while hot.

Calcium pentasulphide CaS_5 is formed when the monosulphide or hydrate of calcium is boiled for a long time with excess of sulphur. Concentrated solutions of calcium hydrosulphide $Ca(HS)_2$ also react energetically upon powdered roll sulphur; on preventing access of air by performing the operation in a current of hydrogen, an orange-red solution is produced with fall of temperature, and on warming the calcium is completely converted into CaS_5. The reaction is reversible, a current of sulphuretted hydrogen causing deposition of sulphur and reformation of hydrosulphide.

Auld obtained evidence indicating the possible existence of polysulphides as high as CaS_7, and suggests the constitution



the atoms of sulphur in the chain becoming progressively more loosely attacked. (For the chemical composition of lime-sulphur animal dips, *see* Chapin, U.S.A. Dept. Agric. Bull. 451, 1916).

Calcium oxysulphides. When calcium hydroxide is used as above, besides CaS_5 there is also formed an oxysulphide of the composition $5CaS{\cdot}CaO,20H_2O$ (Rose). The same substance is obtained in gold-coloured needles when the solution obtained by boiling crude calcium monosulphide with much water is evaporated.

According to Hoffmann (Compt. rend. 62, 291), a mixture of two molecules of calcium monosulphide and one molecule lime at a red heat, forms the oxysulphide $2CaS{\cdot}CaO$. This oxysulphide is contained in recently lixiviated soda residues.

Geuther (Annalen, 224, 178) obtained crystals of $CaS_5{\cdot}2CaO,10H_2O$ by boiling sulphur in milk of lime. They dissolve in hydrochloric acid, forming hydrogen persulphide H_2S_5, and a little H_2S. On boiling calcium monosulphide and sulphur with water, crystals of $CaS_5{\cdot}3CaO,15H_2O$ were obtained. Divers obtained a compound of the formula $11CaS{\cdot}5CaO$ by igniting lime in a mixture of carbon dioxide and carbon disulphide.

Auld (Chem. Soc. Trans. 107, 480), by boiling together lime and sulphur in proportions calculated to give the disulphide obtained in each case Herschell's crystals, for which he proposes the formula $CaO,CaS_2,7H_2O$. A lime sulphur wash, used as a fungicide, is prepared by boiling together one part of quicklime, two or more parts of sulphur, and ten parts of water. The concentrated commercial product contains calcium polysulphides and thiosulphate, generally with minor proportions of sulphite and sulphate.

Calcium sulphydrate $Ca(HS)_2$ is formed together with the hydroxide when the monosulphide is boiled with water. The best mode of preparing it is to pass sulphuretted hydrogen through the hydroxide or sulphide suspended in water, with constant agitation, until it ceases to be absorbed. It is difficult to obtain in the solid state, being decomposed, when the stage of crystallisation is reached, into SH_2 and CaS which separates in silky prisms.

Divers (Chem. Soc. Trans. 1884, 270) obtained it in the solid form by forcing sulphuretted hydrogen through semi-solid calcium hydroxide and water so as to obtain a saturated solution of the sulphydrate. Air was excluded, and, on settling, decanting in a stream of H_2S, and cooling by ice, crystals formed in abundance. They were colourless prisms, melting on slight rise of temperature with partial decomposition. They readily dissolved in a fourth of their weight of water, and could not be removed from the atmosphere of sulphuretted hydrogen without decomposition. They possessed the formula

$$CaH_2S_2,6H_2O.$$

Calcium sulphydrate may be used as a depilatory. If sulphuretted hydrogen be passed into thin milk of lime till the mass acquires a bluish-grey colour, the paste thus formed, when thinly laid upon the surface from which the hair is to be removed, permits of the ready removal of the hair a minute or two afterwards by scraping with a dull knife. It has been proposed to employ it in the tan-yard.

Calcium hydroxy-sulphydrate $Ca(SH)(OH)$ is formed, according to Divers, by action of water upon the crystals of the last-described salt:

$$Ca(SH)_2+H_2O = Ca(SH)(OH)+H_2S.$$

Also by union of water with calcium sulphide, as in interior of heaps of soda waste; and by reaction between $Ca(OH)_2+H_2S$ in the coal-gas purifier. Exposed to air, crystals of $Ca(HS)_2$ are rapidly converted to $Ca(SH)OH$, and concentrated solutions of the sulphydrate exposed to air become rapidly covered with crystals, and an abundant crop of crystals of $Ca(SH)OH$ is obtained on passing in a current of air. The crystals are colourless four-sided prisms of silky lustre, easily obtained dry, of the composition $Ca(SH)OH,3H_2O$. They slowly evolve SH_2 in air, and become yellow by absorption of oxygen They are readily soluble in water, but the solution rapidly decomposes into hydroxide and sulphydrate. They are insoluble in alcohol.

According to Folkard (Chem. News, 49, 258), by exposing calcium hydroxide to the action of sulphuretted hydrogen until it ceases to gain weight a grey powder of the composition $4Ca(HO)_2\cdot 3H_2S$ is obtained. By the action of coal gas sulphuretted hydrogen is evolved from it, and at 100° water is eliminated, leaving

$$Ca(OH)_2\,Ca(SH)OH.$$

This greyish-green powder, when gently heated in coal gas, leaves a yellowish-white salt

$$2Ca(HO)_2\cdot Ca(SH)OH\,CaS,$$

and this at a red heat forms $2CaO\cdot Ca(SH)OH\cdot CaS$, which, when ignited in air, burns like tinder to $CaSO_4$.

The lime-sulphur solutions employed as insecticides and plant sprays in agriculture, prepared by boiling together water, lime, and sulphur, consist mainly of calcium polysulphides, calcium hydroxysulphydrate, calcium thiosulphate with sulphur held in solution. For their analysis, *see* Bodnar, Chem. Zeit. 1915, 39, 715; Analyst, 1915, 513; Ramsay, J. Agric. Sci. 1914, 6, 476. The following is an analysis of a typical lime-sulphur spray, sp.gr. 1·3735, the results being expressed in grams per 100 c.c. (Ramsay, *l.c.*):–

	Sulphur.		Lime.
Hydroxy-sulphydrate containing .	0·911	associated with calcium	1·653
Disulphide containing	11·716	„	12·877
Free sulphur .	23·11		––
Thiosulphate containing	0·99		0·86
Sulphate „	0·07		0·11
	30·83		15·50

Calcium sulphocarbonate $CaCS_3$. Lime over which coal gas containing sulphuretted hydrogen has been passed readily absorbs carbon disulphide. Absorption is most complete when the lime is moistened with water; this material, when fouled, is mixed with an equal weight of slaked lime. The absorption of carbon disulphide stops when one-third of the sulphide is converted to sulphocarbonate $CaS+CS_2=CaCS_3$. On exposing the product for a short time to the air, it is again rendered capable of removing carbon disulphide.

On passing hydrogen saturated with vapour of carbon disulphide into a mixture of calcium monosulphide and a little water, the liquid becomes red, and *in vacuo* deposits red prismatic very deliquescent needles of composition

$$Ca(OH)_2\cdot CaCS_3,7H_2O.$$

When the hydroxy-sulphydrate is employed instead of monosulphide, yellow crystals of

$$2Ca(OH)_2\cdot CaCS_3,10H_2O$$

are obtained.

From these facts Veley (Chem. Soc. Trans. 1885, 478) concludes that the carbon disulphide is absorbed by $Ca(SH)OH$, and not by CaS, and that the reactions are as follows:—

(1) $CaS+H_2O=Ca(SH)OH.$

(2) $Ca(SH)_2+H_2O=Ca(SH)OH+H_2S.$

(3) $2Ca(SH)OH+CS_2=Ca(OH)_2\cdot CaCS_3+H_2S.$

The basic sulphocarbonate is unstable, being decomposed slowly by sulphuretted hydrogen and readily by carbon dioxide.

When milk of lime is agitated with carbon disulphide, bright orange needles of a basic sulphocarbonate $Ca(HO)_2\cdot CaCS_3,6H_2O$ are deposited.

Calcium selenides. The monoselenide is formed as a flesh-coloured precipitate by precipitating calcium chloride with potassium monoselenide. Lime water saturated with seleniuretted hydrogen deposits crystals of calcium selenide when exposed to the air. When lime and selenium are heated just below redness, a polyselenide mixed with calcium selenite is formed.

Calcium sulphite $CaSO_3$ is formed when a solution of an alkaline sulphite is added to the solution of a calcium salt: it is a white powder soluble in 800 parts of water. It dissolves in sulphurous acid, and the solution on exposure to air deposits six-sided needles of the composition $CaSO_3,2H_2O$.

The solution in sulphurous acid is known commercially as bisulphite of lime, and is manufactured by passing sulphur dioxide into milk of lime. In Kynaston's process (Pat. 15659, 1884) a mixture of calcium chloride solution, magnesia, and a little carbonate of lime is brought into contact with sulphur dioxide. The SO_2 is caused to ascend a flagstone tower packed with pigeon-holed brickwork, while the mixture is allowed to run down the tower in such proportions, that from the base there runs a mixture of neutral calcium sulphite, suspended in a solution of magnesium chloride containing the excess of sulphurous acid. The sulphite is settled out in tanks, the supernatant liquor drawn off and concentrated to 40°–45°Tw.; then a quantity of alkali waste is added to it in a closed iron vessel, and the whole heated, when sulphuretted hydrogen is given off, and calcium chloride, magnesia, and calcium carbonate with alkali cinders remain. The latter are removed in a strainer, and the emulsion is ready to be again treated with sulphur dioxide. The whole of the calcium carbonate present is converted to sulphite, carbon dioxide being evolved.

According to Birnbaum and Wittich (Ber. 13, 651), calcium oxide does not absorb sulphur dioxide gas below 400°, but at this temperature combination takes place rapidly with formation of a basic sulphite $Ca_6S_5O_{16}$ or $6CaO\cdot 5SO_2$. At 500° the gas is rapidly absorbed, but the sulphite splits up into sulphate and sulphide.

Calcium sulphate $CaSO_4$ is frequently found in limestone rocks or in company with common salt in the anhydrous state as the mineral *anhydrite*. Anhydrite occurs both in rhombic crystals and in a semi-crystalline massive form. Clear colourless crystals are coloured blue by exposure to radium, and are slightly phosphorescent when heated. More frequently the sulphate is found hydrated as *gypsum* $CaSO_4,2H_2O$, of which the well-crystallised form is termed *selenite*, a fibrous variety *satin spar*, and a finely crystallo granular form *alabaster*. Selenite occurs in fine monoclinic prisms, frequently twinned in characteristic arrow head shapes.

Gypsum is found in the Keuper marls in Nottinghamshire, and at Chellaston in Derbyshire. Selenite crystals exposed to radium are occasionally coloured, in parts, a faint smoky brown.

The anhydrous sulphate may be artificially obtained in crystals resembling anhydrite, of sp gr. 2·9, by fusing calcium chloride with excess of potassium sulphate (Manross, J. 1852, 9).

Hydrated calcium sulphate is precipitated on adding dilute sulphuric acid or a soluble sulphate to an aqueous solution of calcium chloride. The sp gr of gypsum is 2·31. When it is heated to 100°–200° it gives up three fourths of its water rather quickly, but it requires a temperature of 200°–250° to expel the remainder. Dried at 100°, the hydrate $2CaSO_4,H_2O$ of sp gr. 2·7 is left. The anhydrous salt fuses at a red heat without decomposition, and on cooling, assumes the structure of anhydrite. When dehydrated calcium sulphate is pulverised and mixed with water, it absorbs two molecules of water, and solidifies to a very hard mass with evolution of heat, expanding in so doing so as to fill any mould in which it is cast, due probably to the outward thrust of the lath shaped crystals of the hydrated salt during growth; hence the use of gypsum or plaster of Paris in preparing casts. If the gypsum has been heated to a little over 200°, thus being deprived of all its water, it becomes dead burnt, and takes up water very slowly and without hardening.

Calcium sulphate is very slightly soluble in water, the anhydrous sulphate being nearly insoluble. The solubility of the hydrate attains a maximum at 35°, one part dissolving in 393 parts water (Poggiale); at 0° in 488 parts, and at 100° in 460 parts. The solubility is increased by presence of hydrochloric or nitric acids, or chlorides of ammonium or sodium, hence its presence in salt springs; probably in most cases partial double decomposition has occurred.

According to Lunge (J. Soc. Chem. Ind. 1885, 31), the solubility of calcium sulphate in solutions of sodium chloride increases with the percentage of salt, but diminishes with increase of temperature.

At 21·5°, 100 c.c. of a 3·53 p.c. solution of NaCl dissolves 0·5115 gram $CaSO_4$.

At 18·0°, 100 c.c. of a 14·18 p.c. solution of NaCl dissolves 0·7340 gram $CaSO_4$.

At 101·0°, 100 c.c. of a 3·53 p.c. solution of NaCl dissolves 0·4891 gram $CaSO_4$.

At 102·5°, 100 c.c. of a 14·18 p.c. solution of NaCl dissolves 0·6248 gram $CaSO_4$.

Calcium chloride diminishes the solubility of $CaSO_4$ the more it is concentrated, but at the boiling-point the concentration is immaterial. Hydrochloric acid increases the solubility both with increase of concentration and of temperature.

Gypsum is readily soluble in excess of sodium thiosulphate, forming calcium thiosulphate, which combines with the excess of the sodium salt to form a soluble double thiosulphate. On addition of alcohol, this double salt separates as a thick heavy liquid, which solidifies, forming needle-shaped crystals.

Both calcium and barium sulphate can be conveniently and quantitatively reduced at a temperature of 900°–950° by means of a dry current of carbon monoxide. Reduction commences at 680°–700°, becomes vigorous at 750°–850°, and is practically finished at 900°. The reduction with carbon in an atmosphere of nitrogen begins at 700°, is vigorous at 800°–900°, and is complete at 1000° (Bull. Amer. Inst. of Min. Eng. 1910, 917).

A large experimental plant for utilising, in Germany, the dumps of calcium sulphate resulting from the neutralisation of excess sulphuric acid in the sulphonation processes, consists in mixing the presscake with coal and a slagging material, presumably of the composition required to give a cement mixture; this is fed into a type of rotary kiln 50 metres long and 3 metres in diameter which is coal dust fired. The fumes containing sulphur dioxide are cleaned from dust by electrostatic means (unsatisfactory at the time) and are passed into the sulphur trioxide converters. The cement produced from the clinker is of satisfactory quality. (J. Soc. Chem. Ind. 287, 19[illegible])

Calcium sulphate cements. Gypsum, hydrated calcium sulphate $CaSO_4,2H_2O$, is the source of this class of cements, which depend for this property of setting on the reacquisition of the water associated with calcium sulphate in gypsum.

The chemistry of calcium sulphate cements, though much the simplest of that concerned with cements depending for their setting on hydration, is of considerable difficulty, and its present condition is far from definitive. Putting aside controversial views, the situation may be summarised thus: When $CaSO_4,2H_2O$ is heated, it loses water, and at a temperature of about 107° becomes converted into the hemi-hydrate $2CaSO_4,H_2O$. When this substance is mixed with water, it is hydrated, and reforms $CaSO_4,2H_2O$, which crystallises first in the orthorhombic, and finally in the monoclinic, system. The quantity of water sufficient to bring the hemi-hydrate back to the fully hydrated condition is much smaller than is necessary to dissolve it; but, nevertheless, complete crystallisation is accomplished thus: the hemi-hydrate readily forms a supersaturated solution, from which not it but the dihydrate is deposited. The water thus released dissolves another portion of the hemi hydrate, and the process of deposition is repeated indefinitely until, provided there was originally enough water to transform $2CaSO_4,H_2O$ into $CaSO_4,2H_2O$, the whole of the former will have been dissolved in detail and deposited in detail in the shape of the latter. As stated in the section dealing with Portland cement, it is believed that this formation of a supersaturated solution, deposition of the surplus dissolved material, and re-use of the water for the solution of another fraction of the material is general for cements which set when mixed with water, and, although there are many gaps in the proof, yet the hypothesis is useful. In the case of calcium sulphate cements, it may be regarded as well established.

The hemi-hydrate $2CaSO,H_2O$, constitutes plaster of Paris. If gypsum is heated to a higher temperature, *e.g.* above 130°, it becomes completely dehydrated, and yields $CaSO_4$. It appears that $CaSO_4$ can exist in two or more modifications, which behave differently with water As all eventually become hydrated, but not all will set as plaster of Paris, it is probable that only those which will set possess the characteristic property of forming a supersaturated solution, and allowing the mass to crystallise in stages in the manner described above. Keene's cement and Estrichgips (flooring plaster) are examples of cements consisting substantially of anhydrous calcium sulphate. Their setting is influenced by both the temperature at which they have been burnt and by the presence in them of small quantities of substances other than $CaSO_4$, the *modus operandi* of which is exceedingly obscure. In whatever way they are prepared, the final product of setting is $CaSO_4,2H_2O$.

Keane (J. Phys. Chem. 1916, 20, 701) shows that on heating gypsum with slow rise of temperature and constant stirring a halt occurs in the rise of temperature at 90° C., and under some conditions another halt at 139°. There is also an inversion into plaster of Paris $(CaSO_4)_2,H_2O$ at 107° and 971 Hg. pressure, though the temperature may be raised to 200° without this inversion being complete. In German practice the maximum temperature employed is 130°, in English practice 110°–120°, and in American 200° may be reached. These differences are possible because of the rate influence of time and temperature on the inversion and the slowness with which gypsum and plaster develop their true vapour pressures. The same author considers there is only one modification of anhydrous calcium sulphate, but that its properties vary with the degree of agglomeration, and these with the method of formation. The setting of plaster may be retarded by adding flooring plaster, colloids, or any substance which will decrease the solubility of the gypsum and increased by adding substances which increase the solubility.

The manufacture of plaster of Paris is conducted by heating the mineral gypsum to a temperature above that necessary to remove ¾ of its water of crystallisation, and below that requisite to dehydrate it completely. Several methods of burning are in use, ovens, kettles, and rotatory kilns being employed. In English practice a simple oven of the kind shown (Figs. 10 and 11) is adopted, the gypsum in lumps being piled on arches in which the fuel is burnt. In the United States the common plan is to grind the gypsum first, and heat it in a large iron pot or kettle set in brickwork and heated from below. This method is known as 'boiling,' owing to the fine material being kept in a state of agitation by the escaping steam. During the process the powdered material is stirred by an agitator driven by power. A superior quality of plaster is produced, but the method is slow and expensive, and is gradually being abandoned in favour of the rotary calciner.

In Scanegatty's oven the interior is divided by an arch about a foot from the floor, upon the under side of which play the flames from a furnace connected with a lower chamber, the hot air and gases passing afterwards through apertures into the gypsum chamber. The aqueous vapour passes away by a chimney at the top of the oven.

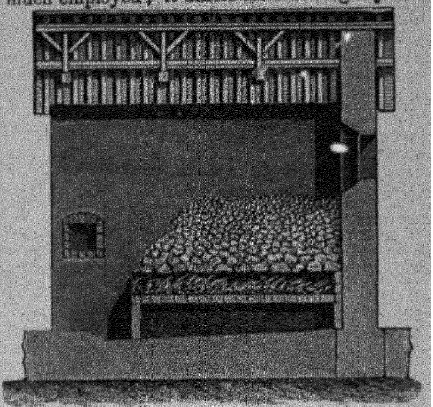


FIG. 10.

Dumesnil's oven is a form which has been much employed; it differs from Scanegatty's in the peculiar arrangement of the lower fire-room, which has twelve openings, the lower blocks of gypsum being arranged so as to facilitate the circulation of the draught from these. The firing is continued for about 4 hours, then the heat is increased for 8 hours, when all openings are closed, and 5–6 cubic metres of coarse gypsum powder spread equally over the top of the burning sulphate. By this means considerable saving of fuel is effected. After standing 12 hours to cool, the contents of the kiln are removed. It is mostly in a state of powder, and the pulverisation is completed by grinding in a stamp or roller mill. The powder is then sifted and stored in a dry place.

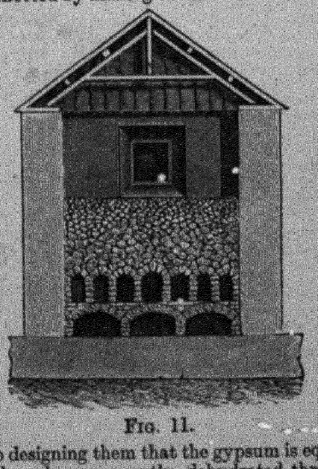


FIG. 11.

Many improvements on the old forms have been effected by making the furnaces continuous, and so designing them that the gypsum is equally heated, and, consequently, dehydrated throughout. This end is also ensured by grinding the gypsum before calcination. The types of ovens employed are very numerous. That of Petry and Hecking, Dortmund, is a rotary kiln, with mill and furnace arranged similarly to those of a cement works. The barrel oven of Perin of Paris is a revolving cylinder, supported upon hollow trunnions, one of which serves for the entrance of the heated gases from the furnace, and the other for exit. The charging is performed from a hopper placed above through a trap-door in the side of the cylinder, which similarly serves to discharge the material when burnt. The Mannheim calciner is provided with a pre-heating chamber, which is placed above the rotating cylindrical furnace. The crushed gypsum is passed through the former by means of a worm conveyor and then into the rotating cylinder, whilst the hot gases from the furnace pass in the opposite direction. In the Cummer rotary calciner, which is much used in the United States, the rotating cylinder is surrounded by a brick chamber, into which the hot gases first pass, and are reduced to a suitable temperature by cold air through inlets in the walls before passing through the calciner. Other ovens are made stationary, but are provided with revolving screws or vanes, which serve to keep the ground gypsum in constant motion, and also to discharge it. Some ovens are heated by means of superheated steam.

In all cases the temperature must be carefully regulated so that only the hemi-hydrate is obtained. On account of the fact that a considerable quantity of water has to be driven off, the temperature of the source of heat may be and in practice is considerably higher than 107°, but the temperature of the mass of gypsum must not be allowed to rise above this, lest complete dehydration occur.

Plaster of Paris varies in composition according to the purity of the gypsum from which it is made. The following analyses are illustrative, and for comparison the composition of the hemi hydrate is appended:—

—	$2CaSO_4,H_2O$	Commercial plaster of Paris	
		1	2
	p.c.	p.c.	p.c.
Calcium sulphate ($CaSO_4$)	93·8	94·53	83 55
Water (H_2O)	6·2	4·12	6·67
Silica (SiO_2)	—	—	4·27
Alumina and ferric oxide ($Al_2O_3+Fe_2O_3$)	—	0·57	0·47
Calcium carbonate ($CaCO_3$)			3·07
Magnesium carbonate ($MgCO_3$)	—	—	1·47

Keene's cement is usually made in this country by first burning the gypsum to the condition of plaster of Paris, dipping the lumps in a solution of alum or of aluminium sulphate, and reburning at a temperature of about 500°, the operation being conducted in ovens in which the fuel is prevented from coming into contact with the material, so as to avoid discolouration. The following is a typical analysis of Keene's cement of good quality:—

	Per cent.
Silica (SiO_2)	**trace**
Alumina (Al_2O_3)	**trace**
Lime (CaO)	**42·04**
Magnesia (MgO)	**trace**
Sulphuric anhydride (SO_3)	**53·54**
Carbonic anhydride (CO_2)	**1·37**

It will be seen that Keene's cement is almost chemically pure $CaSO_4$, the quantity of added matter, such as alum, being negligible. As mentioned above, the function of this and similar additions is obscure, and even the necessity for their use appears doubtful because flooring plaster (*Estrichgips*) is made by burning pure gypsum at about 500°, and, though destitute of alum and the like, sets well. Mack's cement is produced by adding calcined sodium sulphate or potassium sulphate to the completely dehydrated gypsum. Martin's cement is prepared like Keene's, but a solution of potassium carbonate replaces the alum.

There are many different qualities of plaster, but all are of the type of plaster of Paris, or of Keene's cement. The former set in a few minutes, whilst the latter take several hours, and as the rate of setting of plaster of Paris is inconveniently rapid for some purposes, 'retarders,' consisting of such organic substances as glue, blood, and vegetable juices, are often added. These substances of a colloidal nature probably act by obstructing the growth of the crystals of $CaSO_4,2H_2O$, and thus delaying the process of hydration, and, consequently, the setting.

The chief uses of plasters made from calcium sulphate are for making castings or mouldings for interior decoration, for which their white colour, conspicuous in the purer kinds, and their expansion on setting and causing the production of sharp outlines, peculiarly adapt them. On account of the solubility of calcium sulphate in water, these plasters cannot be used for outdoor work. Minor uses are for making moulds for any material which can be cast at a sufficiently low temperature, for making surgical support for broken limbs, and, as an addition to Portland cement, to lengthen its time of setting.

Acid calcium sulphate $CaSO_4 \cdot H_2SO_4$ is formed by heating the neutral sulphate with strong sulphuric acid to 80°-100°. A portion of the porous mass produced dissolves and separates on cooling in microscopic prisms of the composition above indicated. It is decomposed by water, even the moisture of the air, into gypsum and sulphuric acid.

Calcium sodium sulphate $CaNa_2(SO_4)_2$ occurs native in rhombic prisms as the mineral *glauberite*. It may be obtained in the same form by fusing together calcium and sodium sulphates. On heating 50 parts sodium sulphate (Glauber's salt) with an emulsion of 1 part gypsum in 25 parts water to 80°, crystalline needles of

$$CaSO_4 \cdot 2Na_2SO_4,2H_2O$$

are deposited. On further heating, these crystals are transformed into microscopic rhombohedral crystals of glauberite.

In the Welsh process of manufacturing sodium acetate, during evaporation of the liquor formed by double decomposition of calcium acetate by sodium sulphate, **micaceous spangles of glauberite have been noticed by Folkard (Chem. News, 43, 6) to separate out. This explains why calcium sulphate so tenaciously retains sodium sulphate.**

Calcium potassium sulphate

$$CaSO_4,K_2SO_4,H_2O$$

occurs native in monoclinic crystals as *syngenite*.